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CONTENTS

PAGE

33. Steroid compounds. Part VII. Some observations on the Cope-Knoevenagel condensation of ethyl cyanoacetate with ethyl 2-methyl-2-carbethoxyethyl-*cyclo*pentanone and the stereochemistry of the reduction product.—By N. K. Chaudhuri and P. C. Mukharji 155
34. Time variation of the colour in mixtures of ferric chloride and ammonium thiocyanate.—By B. P. Gyani and Miss Rani Misra 160
35. Steroid compounds. Part VIII. On the stereochemistry of Michael addition to 4 methyl-4-carbethoxy-Δ^2-*cyclo*hexenone.—By P. C. Mukharji ... 167
36. Viscosity of supersaturated solutions of some ionic crystals.—By D. Sri Rama Rao and P. Bhaskara Panicker 171
37. Experiments on the syntheses of furano compounds. Part VI. Self-condensation of *iso*coumaranone. Part I.—By J. N. Chatterjea 175
38. Synthesis of cyanine dyes by the condensation of *p*-dialkylaminobenzaldehyde with appropriate heterocyclic compounds. Part VI.—By M. Q. Doja and Arun Kumar Sinha 183
39. Fries rearrangement of *m*-tolyl arylsulphonates.—By Miss A. A. Aleykutty and V. Baliah 189
40. Complex compounds of cobalt^{III}. Part I. Dipyridino-cobaltic-*bis*biguanidinium hydroxide and its salts.—By S. P. Ghosh and J. N. Gupta 193
41. Separation of methyl esters of fatty acids from their mixtures by urea complexes.—By A. S. Gupta and J. S. Aggarwal 197
42. Effect of non-electrolytes on the antagonism of ions in coagulation of hydrophobic sol.—By L. Pochhali and S. N. Mukherjee 201
43. Reduction of mercuric chloride by oxalic acid in the dark in presence of potassium permanganate as inductor.—By C. Prasad and Abani K. Bhattacharya ... 205
44. Studies on the gelation of silicic acid sols. Part III. Cationic and anionic effects on the time of gelation.—By K. C. Sen and B. N. Ghosh 209
45. Search for new antibacterial compounds. Part I.—By S. S. Tiwari and Brajendra N. Tripathi 211
46. Search for new insecticides. Part II.—By S. S. Tiwari and Brajendra N. Tripathi 214
47. The phase-diagram studies of the binary systems. Part II. Salol-diphenyl, salol-acenaphthene and salol-phenanthrene.—By D. K. Majumdar ... 217
48. Studies on metal ferrocyanides. Part I. Volumetric determination of cadmium by ferrocyanide.—By G. S. Deshmukh and M. Venugopalan ... 222

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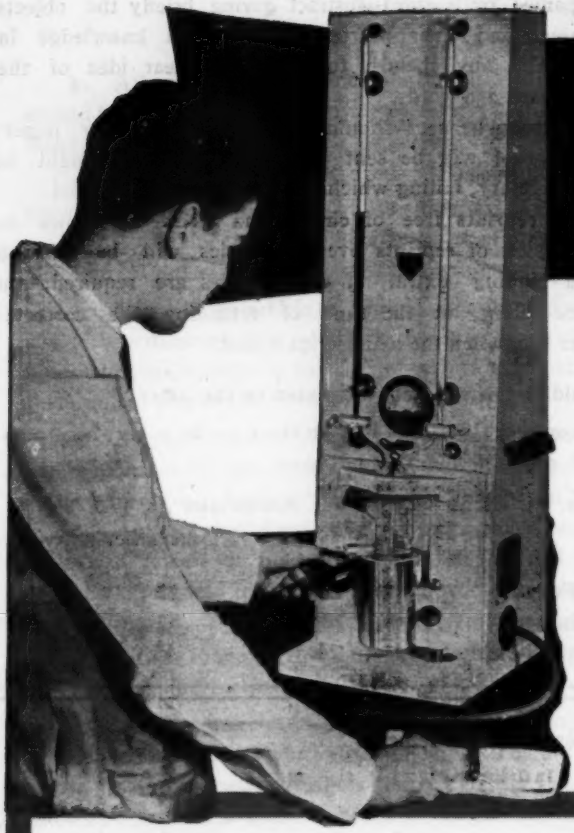

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[Jour. Indian Chem. Soc., Vol. 33, No. 3, 1956]

STEROID COMPOUNDS. PART VII *. SOME OBSERVATIONS ON THE COPE-KNOEVENAGEL CONDENSATION OF ETHYL CYANOACETATE WITH ETHYL 2-METHYL-2β-CARBETHOXYETHYL*cyclo*PENTANONE AND THE STEREOCHEMISTRY OF THE REDUCTION PRODUCT

By N. K. Chaudhuri and P. C. Mukharji

The stereochemistry of the cyanoacetic ester derivative (III), described in Part I, has been established by conversion to the *cis*-ketone (IX). The abnormal product, reported earlier, has been fully characterised and its structure established.

In Part I of this series (Mukharji, this *Journal*, 1947, **24**, 91) the preparation of the cyanoacetic ester derivative (III) was described. This was obtained by reduction of the corresponding unsaturated compound (II) with aluminium amalgam and from the above saturated derivative, (III), the synthesis of the tricyclic compounds (VI and VII) was carried out. The stereochemical course of the entire reaction sequence depends on the stereochemistry established during the reduction of the unsaturated ester (II) to the saturated ester (III).

The choice of the particular synthetic approach, described in Part I, was influenced by the observation of Linstead that reduction of ethyl (2-methyl-2-carbethoxy)-*cyclo*-pentylidene-cyanoacetate (IV) with aluminium amalgam furnished the *trans*-isomer of the corresponding dihydro-ester (V) (Errington and Linstead, *J. Chem Soc.*, 1938, 666). We anticipated similar course in our compound to yield the *trans*-isomer of (III), thereby establishing the *trans* configuration in the union of the C/D rings in our synthetic system, identical with that present in natural steroids. The experiments described in the present communication, however, confirm that the reduction of (II) leads exclusively to the *cis*-isomer of (III), and in view of this result the synthetic approach, described in Part I, is of no value for the total synthesis of steroids. The work reported in this paper was completed some years back, but publication had been delayed due to some unavoidable difficulties.

The saturated cyano-ester (III) (Mukharji, *loc. cit.*) was hydrolysed with concentrated hydrochloric acid to the dibasic acid (VIII: R=H) which proved to be completely homogeneous. It was next converted into the diethyl ester (VIII: R=Et) and then subjected to the Dieckmann condensation with sodium dust in anhydrous benzene. The resulting β-keto-ester was hydrolysed to the hydrindanone (IX). This ketone readily furnished a semicarbazone, m.p. 191-92° and a 2:4-dinitrophenylhydrazone, m.p.125-26°.

A ketone of this structure, provisionally assigned the *cis* configuration but without any proof, had been described by McQuillin and Robinson (*J. Chem. Soc.*, 1938, 1097). They prepared it by catalytic reduction of the eneone (X) and

* Continuation of Part I.

characterised it by a semicarbazone, m.p. 191°. Although a direct comparison was not made, the two ketones, obtained differently, appeared to be identical. An authentic synthesis of *cis*-8-methyl-5-ketohydrindane has been described recently by Conroy (*J. Amer. Chem. Soc.*, 1952, **74**, 3045) which he characterised by a 2:4-dinitrophenylhydrazone, m.p. 126-28°.

Through the courtesy of Dr. Conroy we were able to secure a sample of his derivative and compare it with ours. A mixed melting point determination of the two hydrazones did not show any depression of melting point and confirmed the identity ot the two ketones. The *cis* configuration of our ketone was thus established and, hence, that of the cyano-ester (III).

In Part I it was also mentioned that during condensation of ethyl cyanoacetate with the keto-ester (I : R = Et) in presence of ammonium acetate, an abnormal product (m.p. 121°) was obtained besides the normal condensation product (II). This was a highly crystalline nitrogenous substance, which gradually turned into a brown oil and finally polymerised on standing. The structure of this compound, as represented by (XI), has been established through the following observations :

(*a*) The compound, which was neutral, analysed for $C_9H_{13}ON$.

(*b*) Hydrolysis with dilute acid afforded 2-methyl*cyclo*pentanone-2β-propionic acid (I : R = H), identified as the semicarbazone of its ethyl ester (II : R = Et) and direct comparison with an authentic sample.

(*c*) The same compound was formed when the keto-ester (I : R = Et) was heated with ammonium acetate and acetic acid in benzene solution under identical conditions.

(*d*) It could be prepared by hydrolysis of 2-methyl-2β-cyanoethyl*cyclo*pentanone (XIII) with 80% sulphuric acid at room temperature, the intermediate amide undergoing ring-closure to yield (XI) (cf. Albertson, *J. Amer. Chem. Soc.*, 1952, **74**, 3816; Bruson and Reiner, *ibid.*, 1948, **70**, 214).

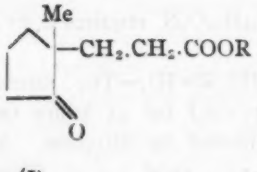
The above facts, however, do not permit of an unequivocal decision between the two possible alternative structures (XI and XII) for this compound. A decision in favour of (XI) was obtained through study of the infra-red spectra of the compound. It showed a sharp band at 2.95μ and a very strong band at 6.05μ, characteristic of an amide with a free-NH group, and another band at 6.1 μ for the $-CH=CH-NH-$ group.

The ultraviolet spectra of the compound showed a maxima at 238 mμ (log ϵ, 4.04). $\alpha\beta$-Unsaturated amines generally show absorption maxima around 228-236 mμ, indicating that the amino group possesses conjugating power, similar to $-C=C-$ by interaction of the unshared electron pair on nitrogen with the π-electron of the double bond (Braude, *Ann. Rep. Chem. Soc.*, 1945, **42**, 105; Bowden, Braude, Jones and Weedon, *J. Chem. Soc.*, 1948, 45; Bowden, Braude and Jones, *ibid.*, 1946, 948; Herr and Heyl, *J. Amer. Chem. Soc.*, 1952, **74**, 3627; 1953, **75**, 1918). Very recently Leonard and Locke (*J. Amer. Chem. Soc.*, 1955, **77**, 438) have studied the ultraviolet maxima of a number of $\alpha\beta$-unsaturated amines and reported the maxima of a very similar compound as ours, 1-*n*-butyl-2-methyl-Δ^2-pyrroline (XIV) at 238 mμ.

If Woodward's rule (*ibid.*, 1942, **64**, 72) be extended to these compounds, the calculated value for the compound (XI) should be about 243 mμ, corresponding to a bathochromic shift of 5 mμ due to an exocyclic double bond. The observed value of 238 mμ is certainly due to acylation of the nitrogen in (XI) which produces this hypsochromic shift due to the opposing effect created by participation of the nitrogen electron pair with the carbonyl group in amide resonance. In β-amino-crotonic ester (λ_{max} , 274 mμ) the absorption maxima is shifted to 269 mμ in the corresponding N-acetyl derivative (Banerjee, Sen Gupta and Das Gupta, *J. Org. Chem.*, 1954, **19**, 1516).

The formation of such byproducts is due to the interaction of free ammonia from ammonium acetate with the carbonyl group (Weiss, *J. Amer. Chem. Soc.*, 1952, **74**, 200, 5193) and such products have subsequently been reported by various other investigators (Sukh Dev, this *Journal*, 1953, **30**, 443; Banerjee, Sen Gupta and Das Gupta, *loc. cit.*).

The preparation of the keto-ester (I : R = Et) has been simplified and considerably improved upon by monocyanoethylation of 2-methyl*cyclo*pentanone in presence of a few drops of 40% methanolic KOH (Frank and Pierle, *J. Amer. Chem. Soc.*, 1951, **73**, 724). This preparation will be reported in detail by one of us (N.K.C.) separately. The yield in the Cope-Knoevenagel condensation of the keto-ester (I:R = Et) with ethyl cyanoacetate was considerably improved by employing Caroge's modification (Caroge, Roble and Sprauge, *J. Org. Chem.*, 1950, **15**, 1388).



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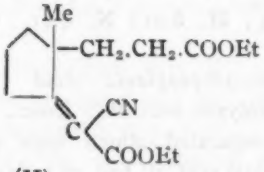

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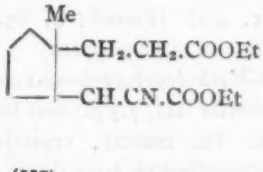

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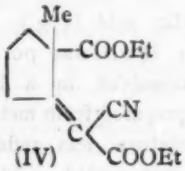

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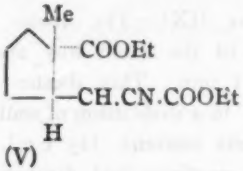

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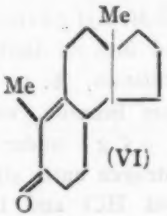

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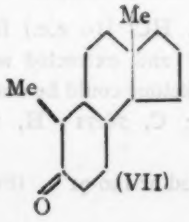

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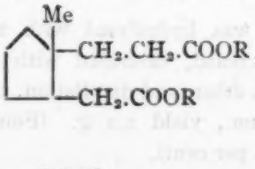

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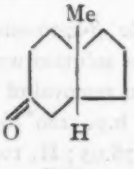

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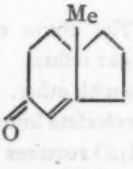

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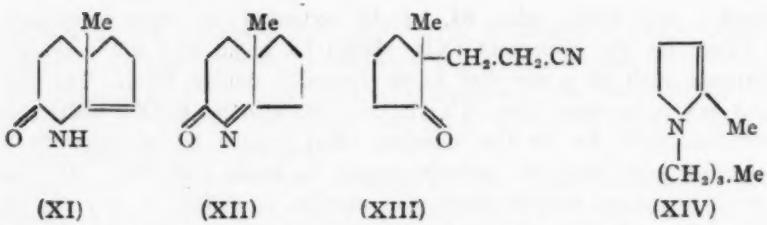

(XI) (XII) (XIII) (XIV)

EXPERIMENTAL

Ethyl 2-methyl-2β-carbethoxyethylcyclopentylidene-cyanoacetate (II) was prepared according to Carcge's modified method in a better yield than previously obtained (Mukharji, *loc. cit.*).

A solution of 2-methyl-2β-carbethoxyethyl*cyclo*pentanone (I : R = Et ; 29.7 g., 0.15 *M*), ethyl cyanoacetate (34 g., 0.3 *M*) and acetic acid (7.5 g., 0.12 *M*) in benzene (60 c.c.) was heated under reflux, fitted with a Dean-Stark water separator. Ammonium acetate (9.5 g., 0.12 *M*) was added in five equal instalments at an interval of 4 hours. After addition of the last portion of the catalyst, the mixture was refluxed for further 8 hours, then cooled, washed several times with water, concentrated and distilled under reduced pressure. After a forerun of unchanged components, the solid byproduct (2.5 g., b. p., 130°-150°/1 mm.) distilled over, followed by a colorless viscous oil (23 g.) which was collected, b.p. 165-67°/1 mm. $\lambda_{max}^{alcohol}$, 240 mμ (log ε, 4.1). (Found : C, 65.25 ; H, 8.01; N, 4.61. $C_{16}H_{23}O_4N$ requires C, 65.53 ; H, 7.85 ; N, 4.78 per cent).

2-Methylcyclopentane-1-acetic-2β-propionic Acid (VIII : R = H).—The saturated cyano-ester (III, 7.5 g.) was hydrolysed with HCl (conc., 30 c.c.) for 45 hours under reflux. On cooling, crystals separated which were collected by filtration. After one crystallisation from dilute acetic acid it had m.p. 152-53°, yield 4.5 g. (Found : C, 61.82 ; H, 8.50. $C_{11}H_{18}O_4$ requires C, 61.68 ; H, 8.41 per cent).

cis-8-*Methyl-5-ketohydrindane* (IX).—The above dicarboxylic acid (4 g.) was converted into its diethyl ester in the usual way and the ester (4 g.) was purified by distillation, b. p. 133-36°/1 mm. This diester (4 g.), dissolved in a little anhydrous benzene, was added to a suspension of sodium dust (prepared from metallic sodium, 0.5 g.) under anhydrous benzene (25 c.c.). The mixture was refluxed under nitrogen until all sodium particles had disappeared. It was cooled, acidified with iced HCl and the benzene layer removed. The residue left on removal of the benzene developed an intense blue colour with ferric chloride in alcohol.

The above crude β-keto-ester was hydrolysed with 10% HCl (10 c.c.) for 15 hours at reflux. The solution was cooled, saturated with salt and extracted several times with ether. On removal of the ether and distillation, the ketone could be obtained as a colorless liquid, b.p. 100°/6 mm., yield 1.2 g. (Found : C, 78.71 ; H, 10.43. $C_{10}H_{16}O$ requires C, 78.95 ; H, 10.52 per cent).

The *semicarbazone* after crystallisation from alcohol melted at 190-91°. (Found : N, 20.18. $C_{11}H_{19}ON_3$ requires N, 20.09 per cent).

The 2:4-*dinitrophenylhydrazone* after crystallisation from alcohol melted at 125-26° and did not depress the melting point of an authentic specimen, m.p. 126-28°, supplied by Dr. Conroy. (Found: N, 16.70. Calc. for $C_{16}H_{20}O_4N_4$: N, 16.87 per cent).

4-*Aza*-5-*keto*-8-*methyl*-$\Delta^{8:9}$-*hydrindene* (XI) was obtained as a byproduct in the Cope-Knoevenagel condensation, as described earlier. It was crystallised from petroleum ether (b.p. 30°-60°) containing a little benzene, m.p. 121-22°; $\lambda_{max}^{alcohol}$, 238 mμ (log ε, 4.04). (Found: C, 71.31; H, 8.9; N, 9.46. $C_9H_{13}ON$ requires C, 71.52; H, 8.61; N, 9.27 per cent).

When a mixture of the keto-ester (I: R=Et; 7.5 g.), acetic acid (1.8 c.c.) and ammonium acetate (4 g.) in benzene (15 c.c.) was heated for about 30 hours and the mixture worked up as before, this product (*ca.* 1 g.) was obtained and after crystallisation from petroleum ether-benzene mixture had m.p. 121-22° alone and on admixture with the sample obtained during condensation, described earlier.

2-Methyl-2-cyanoethyl*cyclo*pentanone (10 g.) was treated with 80% H_2SO_4 (10 c.c.) with efficient stirring and at such a rate that the temperature did not rise above 45°. After stirring it at room temperature for another 5 to 6 hours, the mixture was left overnight and then poured into crushed ice, and extracted with benzene. The benzene extract was washed with dilute bicarbonate solution, water, dried and concentrated. This was then distilled under reduced pressure when the fraction boiling at 135°-140°/1 mm. crystallised in the receiver; upon crystallisation from petroleum ether-benzene mixture it had m.p. 121-22°, both alone as well as on admixture with the sample described above.

The byproduct (5 g.) was hydrolysed with HCl (10 c.c.) for about 10 hours. The organic matter was isolated in the usual way and converted into its ethyl ester, as described before. The semicarbazone, m.p. 80-81°, obtained from this preparation was identical in all respects with the semicarbazone of authentic 2-methyl-2β-carbethoxyethyl*cyclo*pentanone (Mukharji, *loc. cit.*).

The authors wish to thank Dr. H. Conroy for an authentic specimen of the 2:4-dinitrophenylhydrazone of *cis*-8-methyl-5-ketohydrindane.

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TIME VARIATION OF THE COLOUR IN MIXTURES OF FERRIC CHLORIDE AND AMMONIUM THIOCYANATE

By B. P. Gyani and Miss Rani Misra

Changes in the colour of mixtures of ferric chloride and ammonium thiocyanate with time have been investigated directly with the help of a Spekker absorptiometer. At least a part of the colour is temperature-reversible. A spontaneous reduction of ferric to ferrous ions is observed which is not affected by light. Addition of acids intensifies the colour at first, which is followed by a decay, affording somewhat similar absorption-time graphs as solutions which have been subjected to heating. The colour is of course intensified by increasing the ammonium thiocyanate concentration, and the initial rate of decay tends to slow down. There is an abrupt change in the slope of the absorption-time graph and the colour eventually tends to become stable at large concentrations of the thiocyanate. The complex nature of the changes is stressed and it is shown that none of the existing views concerning the nature of the colour or changes in it is adequate to explain all the observations.

A good deal of work appears in the literature concerning the red substance formed by the reaction between ferric and thiocyanate ions. Krüss and Moraht (*Ber.*, 1889, **22**, 2054, 2061) considered it to be $Fe(CNS)_3.9KCNS$, the fading due to dilution being ascribed to dissociation of the double salt. Tarugi (*Gazzetta*, 1904, **34**, 326) gave it the formula $FeH(CNOS)_3$. Stoke and Cain (*J. Amer. Chem. Soc.*, 1907, **29**, 412) considered it to be the simple salt $Fe(CNS)_3$, the fading being due to the reduction of $Fe(CNS)_3$ to $Fe(CNS)_2$. On the other hand, Bongiovanni (*Gazzetta*, 1907, **37**, 472) ascribed it to hydrolysis, $Fe(CNS)_3 \longrightarrow Fe(OH)_3$. Philip and Bramley (*J. Chem. Soc.*, 1913, **103**, 795) appear to be the only workers who followed the changes in mixtures of ferric chloride and ammonium thiocyanate over long periods. They established that some reduction took place on storage and that light did not affect the reaction even after four weeks' exposure.

Schlessinger and van Valkenburg (*J. Amer. Chem. Soc.*, 1931, **53**, 1212) prepared solid $Fe(CNS)_3$ which furnished the same absorption spectrum in water, benzene and ether, being dimeric in the last two, and concluded that the red ion was $Fe(CNS)_6^{3-}$. Bent and French (*ibid.*, 1941, **63**, 568) ussd a spectrophotometer to test the equation

$$\frac{[Fe^{3+}][CNS^-]}{[Fe_m(CNS)_n]} = K$$

and found that if $m=1$, then $n=1$, leading to the formula $Fe(CNS)^{2+}$ for the red ions.

Ricca and Farone (*Gazzetta*, 1946, **76**, 78) studied the mixture conductometrically. They considered that depending upon concentration of ammonium thiocyanate, the mixture contained varying proportions of $Fe(CNS)_3$, $Fe(CNS)_2^+$ and $Fe(CNS)^{2+}$. Frank and Oswalt used a Coleman spectrophotometer. Some more papers have been reviewed in a recent work of Jatkar and Mattoo (this *Journal*, 1954, **31**, 299). These authors have come to the conclusion that depending upon conditions, charged and uncharged complexes of the type $Fe(CNS)_n$ may exist where n may have values from 1 to 6. We have used a Spekker absorptiometer on which colour changes may be followed directly and almost instantaneously, to re-investigate the problem.

EXPERIMENTAL

A stock solution of approximately 0.125 *M* ammonium thiocyanate (I) was prepared. A stock solution of ferric chloride containing 52.3 g. of the salt per litre (which was about ten years old) was used. It is important to specify the age of the solution since we have previously found that the hydrolysis of diluted ferric chloride solutions depends upon the age of the stock solution (this *Journal*, 1954, **31**, 499). This stock solution was diluted 100 times immediately before use (II). Since experiments with soda-glass bottles gave rise to erratic results (perhaps due to leaching of alkali) the mixtures were stored either in Jena glass bottles or in ordinary reagent bottles, coated inside with paraffin wax. One centimetre cells were used and the instrument was set to water = 1.000 with Ilford Spectrum Filter No. 602 (blue) unless specified otherwise.

Effect of Heating.—In one experiment equal volumes of (I) and (II) were mixed and enough water added to obtain an immediate Spekker reading of 0.140, *i. e.* an absorption of 0.860. The mixture was then divided into two portions. One was followed at room temperature on the Spekker (curve A, Fig. 1). The other was heated to boiling and followed similarly (curve B). Fig. 1 shows the plot of absorption against time in minutes. While the cold solution tends to decrease in absorption, the reverse is true of the boiled solution. Similar results were obtained in other experiments in which the proportion of water was decreased. The period taken by the two graphs to approach each other increased as the mixture became more concentrated.

FIG. 1

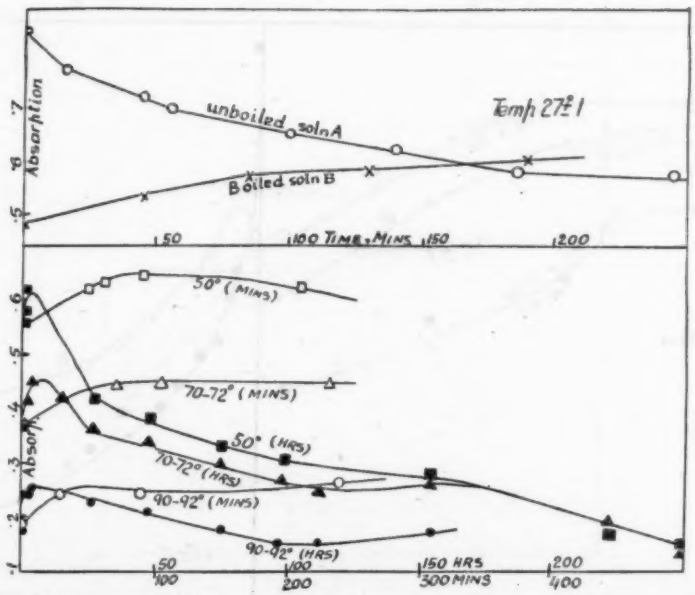
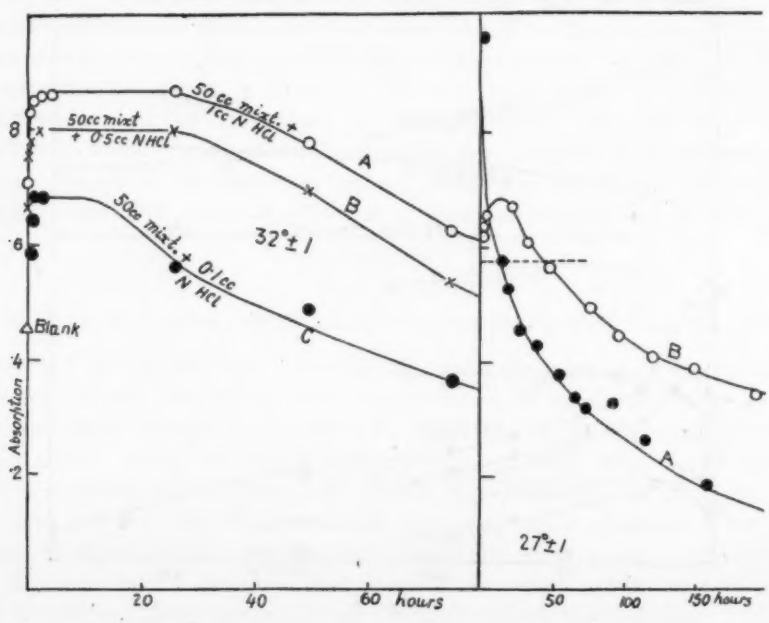


FIG. 2

To investigate this matter further, 40 c.c. of (I) and (II) each and 120 c.c. of water were mixed. The mixture was divided into three portions. These were heated in water-baths rapidly to 50°, 70° and 90° respectively. The heating was stopped as soon as these solutions had attained the specified temperatures. The graphs of absorption against time are shown in Fig. 2. As the temperature is increased the absorption decreases. During the first two hours after heating, the absorption shows a slight increase in each case. Thereafter for the next two hours it is practically constant which is followed by a slow decrease of colour until a more or less steady small absorption is reached, which appears to be nearly constant for all the three curves though they started with quite different intensities of absorption. The view that the fading of colour on storage is produced by hydrolysis of the salt formed at first to ferric hydroxide, or the reduction of ferric ions to ferrous ions, fails to explain the existence of the initial increase.

Effects of Acids and KCl.—In the experiments described below, another stock solution of ferric chloride was used. It contained 46.34 g. of $FeCl_3$ per litre and was a year old. It was diluted 100 times prior to use as before (III). A mixture of 40 c.c. of (I) and (III) each and 120 c.c. of water was taken (initial absorption 0.951) and followed on the Spekker. Curve A, Fig. 3 shows the plot of absorption against time. When the mixture had attained an absorption of 0.558 (dotted horizontal line), 50 c.c. of the mixture was withdrawn and one drop of 2*N*-HCl added. The resulting graph B shows the subsequent changes counting from the moment of addition of the acid. The red colour showed an instantaneous partial recovery, but then declined, though at a smaller rate.

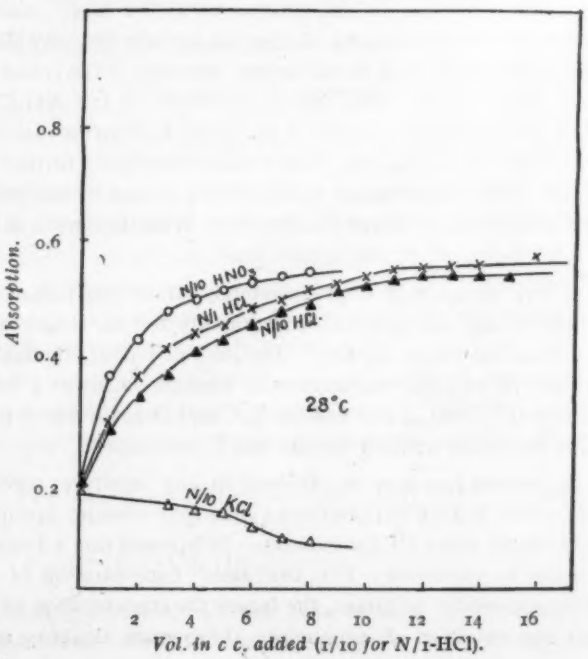
FIG. 4 FIG. 3



A few more quantitative experiments were also carried out. A mixture of 20 c.c. of (I) and (III) each and 110 c.c. of water was prepared (initial absorption 0.470) and divided into three portions. To the first was added 1 c.c. of *N*-HCl (A), to the second 0.5 c.c. (B), and to the third 0.1 c.c. (C). The changes in these mixtures are shown by the corresponding graphs (Fig. 4). There is again observed a rise immediately after addition of the acid. The red colour remains steady for a day if enough acid is present (mixture $N/100$ or above) but an immediate decay may follow if the concentration is less.

The effect on the depth of colour by adding increasing quantities of HCl to a mixture of 5 c.c. of (I) and (III) each and 40 c.c. of water (initial absorption 0.180) has also been studied. At the end of the experiment 1.5 c.c. of $N/1$-HCl had been added in the case of the upper graph and 15 c.c. of $N/10$-HCl in the case of the lower graph (Fig. 5) so that weight of *dry* HCl added along any vertical line in the diagram was always the same. At the end the total volume was 51 5 c.c. in the first case and 65 c.c. in the second. The absorptions in the latter were therefore corrected for dilution, *e g.*, the actual absorption (0.580) corresponding to volume=65 c.c. was multiplied by $65/50$ to obtain the absorption if the volume had remained 50 c.c. Other absorptions were similarly corrected. These corrected values appear in Fig. 5. We note that a maximum absorption is attained in each case which is not increased further after the mixture is a little over $N/50$ in respect of HCl (about 1.2 c.c. *N*-HCl added). If the absorption were determined solely by the weight of dry HCl added, the two graphs should have coincided.

FIG. 5



The addition of HCl in the above two experiments was completed within an hour. In another experiment, in which the addition of HCl was stopped after adding 10 c.c. of the acid and again resumed after two hours, the absorption rose. The concluding portion of the curve was then located higher than the first. This anomaly is easily understood with reference to Fig. 3 or Fig. 4, which show that there is an intensification of colour with the increase in time after addition of the acid. As expected, the colour is found to depend on the manner of adding the acid and also its strength. It is of significance, however, that nitric acid brings about a larger deepening of colour than the corresponding concentrations of HCl, but the final effect is the same. KCl is not indifferent and produces a distinct lowering in the intensity of the colour.

In another series of experiments we prepared a series of mixtures of the compositions, noted below :

A = 5 c.c. of III	+	5 c.c. of 5%	NH_4CNS	+	65 c.c. of	water,	mixture	= 0.042	*N*-NH_4CNS
B = ,,	,,	,,	,,	,,	+ 60	,,	,,	= 0.085	,,
C = ,,	,,	,,	,,	,,	+ 55	,,	,,	= 0.127	,,
D = ,,	,,	,,	,,	,,	+ 50	,,	,,	= 0.170	,,
E = ,,	,,	,,	,,	,,	+ 45	,,	,,	= 0.212	,,

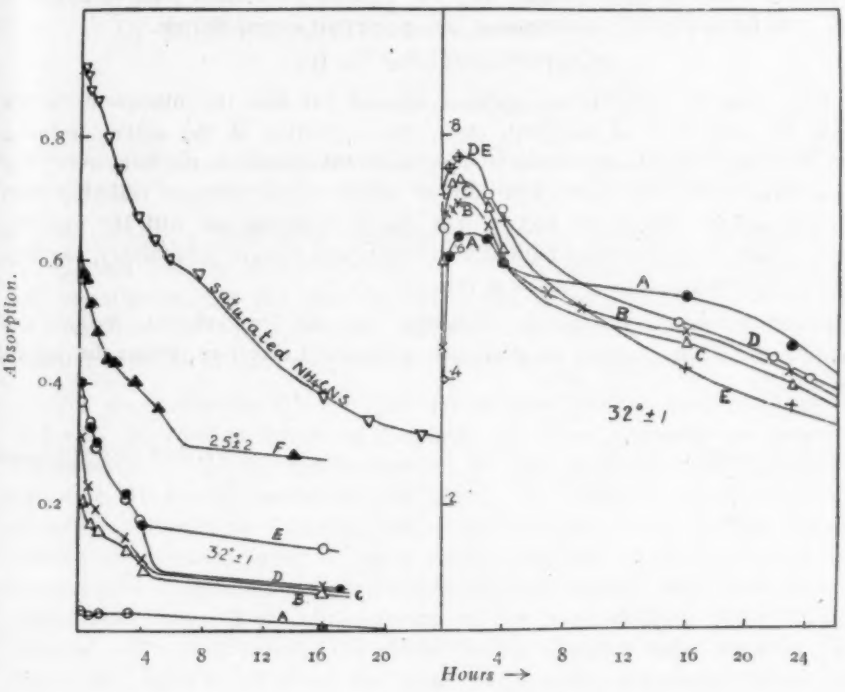
To 50 c.c. of each solution 1 c.c. of *N*-HCl was added. Changes in these mixtures were then followed on the Spekker. Changes in the remaining 20-25 c.c. portions (blanks) were also followed. The results appear in Fig. 6 (blanks) and Fig. 7 (with HCl). It is interesting to note that in the absence of HCl a large concentration of ammonium thiocyanate not only develops a deeper red initially but may also check the decay of colour better. An upper limit to the initial intensity of the colour appears to have been reached at 20 c.c. of 5% NH_4CNS (*i.e.*, about 0.17*N*-NH_4CNS in the mixture). Considering the lower flat portion of the curve E, it seems that a possibility exists that if concentration of ammonium thiocyanate is increased further a stable red colour may be obtained. This expectation is completely belied by the curve F (5 c.c. of III + 70 c.c. of 5% NH_4CNS). Curves for mixtures saturated with NH_4CNS are also shown.

Fig. 7 shows that the presence of HCl completely alters the nature of changes. The intensity of colour in any mixture rises very rapidly at first, a peak is reached in about 1 to 2 hours, followed by a slow decline. The peak is higher, the higher the concentration of ammonium thiocyanate and appears to converge again at a concentration of about 0.17 *N* thiocyanate. During the decline B, C and D again bunch together, but surprisingly enough, A shows the smallest decline and E, the largest.

As fading sets in, ferrous ions may be detected in any mixture whether acid is present or not. Addition of $K_3Fe(CN)_6$ produces a blue coloration or precipitate. The reduction appears to be larger when HCl is present. It appears that a large part of the decline in colour is due to reduction. For the same concentration of HCl in the mixture, the reduction appears to be larger, the larger the concentration of ammonium thiocyanate. A large concentration of ammonium thiocyanate therefore may produce

a large initial intensity of colour, but at the same time gives rise to a larger decline. It may thus be possible to understand the courses of all the graphs in Fig. 7.

FIG. 6 FIG. 7



DISCUSSION

We have established the following experimental facts and any mechanism of production and stability of the red colour would have to account for them : (A) A general slow fading for all solutions irrespective of deepening by any factor; (B) fading of the red colour by temperature increase and slow recovery of the same at lower temperatures; (C) slow reduction to ferrous ions ; (D) intensification of colour by acids, the efficiency being in the order $HNO_3 > HCl$.

It is evident that the existing theories are unable to cover all the present observations nor are our results sufficient to lead to some convincing conclusions. To fix our ideas it is perhaps helpful to write down a scheme for the changes observed such as follows.

$$Fe^{3+} + CNS^- \rightleftharpoons Fe(CNS)_3 \text{ etc. (red)} \longrightarrow \text{unknown products.}$$

(D) (B) (A), (C)

$FeOH^{2+}$, $Fe(CNS)_2OH$ etc.

The letters correspond to the observations noted above. Heating produces enhanced hydrolysis (action B) and depresses the colour. Addition of acid depresses

the hydrolysis in the first instance (action D) followed by the formation of $Fe(CNS)_3$ etc. and restoration of colour. It is not possible at this stage to say whether the observations under (A) and (C), viz., a general slow fading and reduction of ferric ions, are identical. Perhaps these actions may be irreversible. They lead to unknown products. As far as $FeOH^{2+}$ is concerned, it appears that action (B), viz.

$$FeOH^{2+} + \text{acid} \rightleftharpoons Fe^{3+} + H_2O$$

should take place immediately on addition of acid [as also the subsequent reaction leading to the formation of $Fe(CNS)_3$ etc.], but a portion of the action restoring colour is slow (there was always excess of ammonium thiocyanate in the mixture). The actual mechanism may therefore not be quite so simple. The stronger restoring effect of nitric acid may be due to the fact that it has no common ion with the reacting materials. These suggestions are naturally tentative and a more satisfactory explanation has to await further work which is in progress.

The authors thank Shri N. L. Vidyarthi for the loan of the Spekker and Dr. A. P. B. Sinha, now of the National Chemical Laboratory, Poona, for helpful discussions.

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STEROID COMPOUNDS. PART VIII. ON THE STEREOCHEMISTRY OF MICHAEL ADDITION TO 4-METHYL-4-CARBETHOXY-Δ^2-*cyclo*HEXENONE

By P. C. Mukharji

Michael addition of diethyl malonate to the *cyclo*hexenone (IV : R=Et) affords an adduct which after hydrolysis and reduction yields *cis*-1-methyl*cyclo*hexane-1-carboxy-2-acetic acid.

In connection with some problem in steroid synthesis, the steric course of the Michael addition of diethyl malonate to 4-methyl-4-carbethoxy-Δ^2*cyclo*hexenone was investigated. At the time this work was undertaken there was no report in the literature of this particular Michael addition, and very little data were available to permit of any prediction about the stereochemical course of the addition.

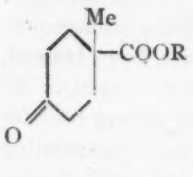
The required eneone (IV : R=Et) was prepared from the easily available keto-acid (I : R=H), described by Rubin and Wishinsky (*J. Amer. Chem. Soc.*, 1946, **68**, 338). The keto-ester (I : R=Et) was brominated in cold and the resulting monobromo derivative (II : R=Et) purified by distillation. The colorless distillate, first obtained, gradually darkened on standing, and analytical values were always erratic. No attempts were made to purify it and a freshly prepared sample was always used for the next step. Attempted dehydrohalogenation with organic bases gave disappointing results and, hence, dehydrohalogenation of the corresponding ketal (III : R=Et) was tried. The cyclic ketal (III) could be readily obtained under standard conditions (Salmi, *Ber.*, 1938, **71**, 1803) and was quite stable unlike the parent bromoketo-ester. On prolonged treatment with potassium *tert.*-butoxide in *tert.*-butyl alcohol (R. Daniels, Ph. D. thesis, Harvard University, 1950), followed by deketalisation according to Schinz and Schappi (*Helv. Chim. Acta*, 1947, **30**, 1483), the unsaturated compound (IV : R=Et) was obtained in a fairly good yield. * This showed strong absorption in the infra-red at 5.8μ and 5.95μ as required for a compound of this structure.

Analysis of the compound, however, furnished high values for carbon, possibly due to *trans* esterification during alkoxide treatment. The eneone (IV : R=Et) with diethyl malonate in the presence of traces of sodium ethoxide at room temperature afforded a viscous adduct (V : R=Et) which was directly hydrolysed in the crude stage with 20% HCl, and the resulting gummy acid was purified in the form of its dimethyl ester. The keto-diester (VI : R=Me), thus obtained, was a colorless mobile oil which gave correct analysis and was characterised by a yellow 2 : 4-dinitrophenylhydrazone. The corresponding dibasic acid (VI : R=H), however, could not be obtained crystalline. To establish the stereochemistry of the

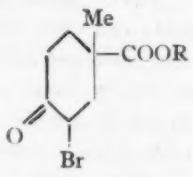
* The learned referee has drawn attention to a recent paper by Wanzlick *et al.* (*Chem. Ber.*, 1955, **88**, 69) who have described a similar procedure for the synthesis of *cyclo*pentenones and *cyclo*hexenones. This paper was not available to the author at the time this manuscript was submitted. The work reported here was completed in the summer of 1951.

product, the above keto-diester was reduced according to Huang-Minlon's procedure (*J. Amer. Chem. Soc.*, 1946, **68**, 2487) to the desoxy-dicarboxylic acid (VII), m.p. 163-64°. Mixed melting point determination with an authentic specimen of *cis*-1-methyl*cyclo*hexane-1-carboxy-2-acetic acid, m.p. 163-64° did not show any depression, whereas on admixture with the *trans*-acid the melting point was considerably reduced (Linstead *et al.*, *J. Chem. Soc.*, 1936, 470, 476, 478; 1937, 1140; Bachmann and Kushner, *J. Amer. Chem. Soc.*, 1943, **65**, 1963; Woodward *et al.*, *ibid.*, 1952, **74**, 4226). No other acid could be isolated from the mother-liquors left after removal of the *cis*-acid. The addition of malonic ester therefore proceeded in a stereospecific manner to yield the *cis*-adduct (V : R = Et).

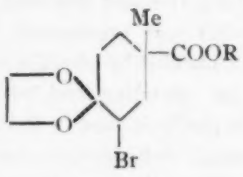
After the completion of this work, Nazarov and Zevyalov (*Chem. Abst.*, 1953, **47**, 10515) described the methyl ester of 4-methyl-4-carboxy-Δ^2-*cyclo*hexenone (IV : R = Me) from the bromo compound (II : R = Me) which they prepared by a different route. The Russian chemists dehydrohalogenated their bromo compound with diethylaniline at 150° and obtained good results. In our hands dehydrohalogenation by this procedure was never satisfactory. Nazarov also added diethyl malonate to the enone (IV:R = Me) and obtained an adduct stereochemistry of which, however, was not defined.



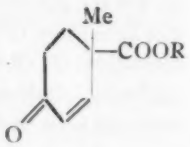
(I)



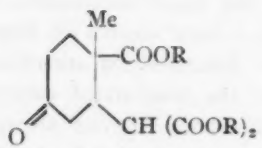
(II)



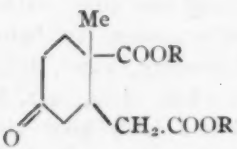
(III)



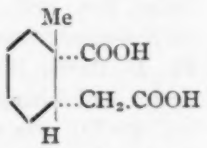
(IV)



(V)



(VI)



(VII)

A plausible explanation for the observed stereospecificity to provide the *cis*-isomer in the above Michael addition may be as follows. In the original *cyclo*hexanone derivative (I), the bulkier carbethoxyl group must be placed in the stable equatorial and the methyl group in the axial position. In the *cyclo*hexenone compound (IV), they will take up the half-equatorial (e′) and the half-axial (a′) positions (Barton, *Chem. Ind.*, 1954, 21). The steric effect is then asserted by the axial (a′) methyl group which directs the incoming malonate anion to approach from the side away from it, and this is perhaps somewhat favoured by the electrostatic attraction of the malonate anion to the side of the carbethoxyl group. The net result is then the axial addition of the malonate group to the ring system, and this picture is in agreement with Corey's bromination experiments in *cyclo*hexanone compounds as well with the theoretical considerations of maximum overlap of the

p-orbitals (Corey, *J. Amer. Chem. Soc.*, 1954, **76**, 175). The reported cases (Abe *et al.*, *Proc. Japan Acad.*, 1954, **30**, 116, 119 ; Ralls, *J. Amer. Chem. Soc.*, 1953, **75**, 2123 ; Shoppee and Stephenson, *J. Chem. Soc.*, 1954 2230), where in the Michael addition the malonate residue has taken up the equatorial position, could be due to thermodynamic considerations, since the Michael addition is a reversible reaction and in the absence of other steric factors operating the more stable isomer with the bulkier group in equatorial position is likely to predominate in equilibrium (cf. Corey, *J. Amer. Chem. Soc.*, 1955, **77**, 1045).

EXPERIMENTAL

Ethyl 4-Methyl-4-carboxy-2-bromocyclohexanone (II : R = Et).—Ethyl 4-methyl - 4-carboxy*cyclo*hexanone (I : R = Et) was prepared from the corresponding keto-acid (I : R = H ; Rubin and Wishinky, *loc. cit.*) in the usual way by esterification with EtOH—H_2SO_4 mixture, b.p. 80°-85°/0.5 mm. (Found : C, 64.91 ; H, 8.77. $C_{10}H_{16}O_3$ requires C, 65.21 ; H, 8.69 per cent).

The above keto-ester (36.6 g.) in dry chloroform (300 c.c.) was cooled in ice and bromine (32 g.), dissolved in chloroform (75 c.c.), was added dropwise with shaking. After the addition was complete the mixture was poured into ice and the chloroform layer removed and then washed with dilute sodium bicarbonate solution, water and dried. The residue, left after removal of the chloroform, was fractionated under reduced pressure. After a forerun of the unchanged keto-ester, the bromo compound distilled at 110°-120°/0.5 mm. as a colorless heavy liquid. On redistillation, the major fraction distilled at 113-15°/0.5 mm., yield 32 g. The initially obtained colorless distillate gradually developed a brown to pink colour which deepened on standing. No satisfactory analysis could be obtained and it was used directly for the next step.

*2-Bromo-4-methyl-4-carbethoxy*cyclo*hexane-1 - spiro - 2' : 1' : 3'-dioxolan* (III : R = Et).—A mixture of the above bromo compound (32 g.), ethyleneglycol (8.4 g.) in dry benzene (160 c.c.) and *p*-toluenesulphonic acid (0.3 g.) was refluxed for 5 hours in a flask fitted with a water separator. The mixture was then cooled, poured into dilute sodium bicarbonate solution and the benzene layer removed, washed with water, dried and concentrated. The residue distilled at 100°-105°/0.3 mm. as a colorless mobile oil, yield 26 g. The ketal was quite stable and did not develop any coloration on standing. (Found : C, 47.58 ; H, 6.35. $C_{12}H_{19}O_4Br$ requires C, 46.90 ; H, 6.18 per cent).

Ethyl-4 - methyl-4- carboxy - Δ^2-cyclo*hexenone* (IV : R = Et).—To a solution of potassium *tert.*-butoxide, prepared from metallic potassium (3.2 g.) and *tert.*-butyl alcohol (70 c. c.), the above bromoketal (III, 25 g.) was added all at once and the mixture refluxed under nitrogen for 40 hours. At the end of this period the dark liquid was concentrated under reduced pressure, cooled and poured into water. The organic matter was extracted with ether, and the residue, left after removal of the ether, was heated for 3 hours with dry acetone (150 c.c.) and *p*-toluenesulphonic acid (0.5 g.). Acetone was then distilled off, the residue poured into water, extracted with ether several times and the combined ether extract washed with dilute sodium bicarbonate solution, then with water and finally dried over anhydrous sodium

sulphate. The residue obtained after removal of ether distilled as a colorless mobile liquid, b.p. 80°-85°/0.3 mm., yield 10 g. A small fraction was redistilled and the middle cut collected for analysis. {Found : C, 67.04 ; H, 8.63. $C_{10}H_{14}O_3$ requires C, 65.93 ; H, 8.78 and $C_{12}H_{18}O_3$ [IV : R = C(CH$_3$)$_3$] requires C, 68.57 ; H, 8.57 per cent}. Sharp bands in the infra-red at 5.8μ and 5.95μ correspond to the ester and the *cyclo*hexenone grouping. A red 2 : 4-dinitrophenylhydrazone was formed, but it separated as a gum and could not be easily obtained crystalline.

cis-*Dimethyl*-4 - *methyl*-4 - *carboxy*cyclo*hexanone*-3-*acetic Acid* (VI : R = Me).—The unsaturated ester, obtained above (9.5 g.), was added to an ice-cold mixture of diethyl malonate (10 g.) and sodium ethoxide in absolute alcohol, prepared from sodium (0.025 g.) and alcohol (15 c.c.). An immediate brown colour developed. The mixture was left overnight at room temperature and then decomposed with ice and acetic acid. The organic matter was taken up in ether and washed with dilute sodium carbonate solution, water and dried over anhydrous sodium sulphate. The viscous residue, left after removal of the ether, could not be distilled owing to decomposition. It was hydrolysed as such with 20% HCl for 20 hours. The aqueous solution was then completely evaporated to dryness and the residual gum esterified with absolute methanol (100 c.c.) and H_2SO_4 (*d* 1.84, 6 c.c.) for 10 hours. The ester was isolated in the usual way and purified by distillation, b.p. 128-30°/0.5 mm. (Found : C, 59 65 ; H, 7.94. $C_{12}H_{18}O_5$ requires C, 59.50 ; H, 7.43 per cent). A higher boiling residue remained in the distilling flask.

The keto-ester readily furnished a yellow 2 : 4-dinitrophenylhydrazone, m.p. 154° after crystallisation from alcohol. (Found : C, 50.92 ; H, 5.69. $C_{18}H_{22}O_8N_4$ requires C, 51.18 ; H, 5.21 per cent). The corresponding dibasic acid (VI : R = H) could not be obtained crystalline.

cis 1-*Methyl*cyclo*hexane* -1- *carboxy*-2-*acetic Acid* (VII).—The above keto-ester (VI : R = Me ; 1 g.), trimethyleneglycol (9 c.c.), hydrazine hydrate (85%, 0.9 c.c.) and powdered KOH (1 g.), intimately mixed, were heated for 2 hours under reflux and then strongly heated without any condenser until temperature of the liquid reached 205°. It was maintained around this temperature for 4 hours and then cooled, diluted with water and poured into iced hydrochloric acid. This was then extracted several times with ether and the ether extract after one washing with water was concentrated. The residual brown gum solidified in contact with a little benzene and scratching. After crystallisation from dilute acetic acid the melting point was 163-64°. Mixed melting point with an authentic sample of *cis*-1-methyl*cyclo*hexane-1-carboxy-2-acetic acid, m. p. 163-64°, was not depressed, but with the *trans*-acid, m. p. 176-77°, the melting point was depressed to 140-42°.

The author wishes to record his thanks to Prof. Gilbert Stork for his interest and for the laboratory facilities provided and to Dr. Franz Sondhiemer for the authentic samples of *cis*- and *trans*-acids.

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VISCOSITY OF SUPERSATURATED SOLUTIONS OF SOME IONIC CRYSTALS

By D. Sri Rama Rao and P. Bhaskara Panicker

Measurements of viscosity of supersaturated solutions of KCl, KBr, KI, K_2SO_4, $K_2Cr_2O_7$, $KClO_3$, NH_4Cl, NH_4Br and $Ba(NO_3)_2$ have been conducted by the method of Scarpa, modified by Taimni. It has been shown that η-T curve for substances like KCl, KBr, KI and K_2SO_4, temperature coefficient of solubility of which is constant, is a straight line and for others such a proportionality is not obtained.

Miers and Issac (*J. Chem. Soc.*, 1906, **89**, 413, et seq) have shown that solutions saturated at a temperature T_s, if cooled, give rise to spontaneous crystallisation at a lower temperature T_c, definite for each substance. In extending this work to a few ionic crystals, Srikantan (this *Journal*, 1950, **27**, 627) has shown that $T_s - T_c$, the limit of supersaturation, is constant for those substances temperature coefficient of solubility of which is constant throughout the range ; substances like NH_4Cl, $KClO_4$, KNO_3 have different values for $T_s - T_c$ at different temperature regions, depending on the solubility coefficient at each range. In the absence of viscosity data of superaturated solutions, Srikantan (*ibid.*, 1952, **29**, 674) has further shown in a semiquantitative way, that

$$(T_s - T_c)(\eta_s - \eta_c) = K,$$

where η_s and η_c are the viscosity of supersaturated solutions at T_s and T_c respectively. Since data on the viscosity of supersaturated solutions were not available (except by Chatterji and Ramgopal, *ibid.*, 1947, **24**, 455) the author had taken the viscosities of concentrated solutions only, thus leading to tentative conclusions. An attempt has been made herein to measure the viscosity of supersaturated solutions of a few ionic crystals and the results have been used to verify the above equation.

Saturated solutions at temperature T_s were cooled through the range $T_s - T_c$, characteristic of each substance, and the viscosity in the range $T_s - T_c$ was measured at different temperatures.

Experimental

The viscosity measurements were made by means of an apparatus devised by Scarpa (*Gazzetta*, 1910, **40**, 261 *) and used by Farrow (*J. Chem. Soc.*, 1912, **101**, 347). Certain modifications were introduced to the above method by Taimni (*J. Phys. Chem.*, 1928, **32**, 604) to prevent the inoculation of the supersaturated solutions with germ crystals carried by dust particles. Further modifications (indicated in Fig. 1) were carried out resulting in greater reproducibility of the results.

The method consists in measuring the time t_1 taken in drawing up, by suction, a sufficient quantity of solution to fill a bulb at the top of a capillary tube, and the time t_2 which this volume of the solution takes in flowing out through the capillary tube

* The paper has been translated from Italian by Mr. G. Martirosi, Italian Chamber of Commerce, Madras-1.

under the action of gravity . Given constant conditions, the viscosity (η) of any liquid, according to Scarpa, is proportional to the expression,

$$\frac{t_1 t_2}{t_1 + t_2} \quad \text{or} \quad \eta = K \times \frac{t_1 t_2}{t_1 + t_2},$$

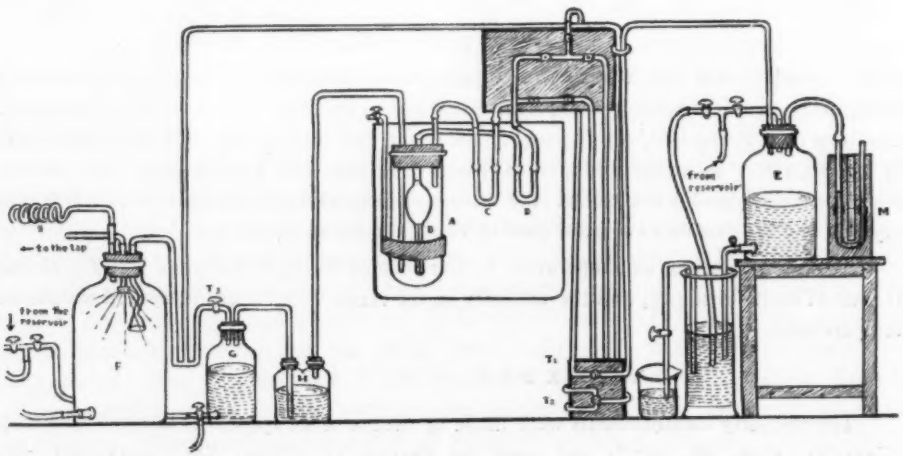
where K is a constant which can be determined by calibrating the viscometer with water. So it is not necessary to measure the dimensions of the viscometer. It has been found that K varies slightly with increase in temperature (Table I).

TABLE I

Pressure (cm.)	...	19	19	25	25
Temp.	...	40°	50°	40°	50°
$K \times 10^3$	...	57.69	56.85	75.51	74.66

However, the great advantage of this method over the ordinary method lies in the fact that it is not necessary to measure the density of the solution, which is an extremely difficult process when dealing with supersaturated solutions. It is immaterial whether equal volumes of solution are used in the different experiments or not.

FIG. 1



The viscometer and the other apparatus used are shown in Fig. 1. 'A' is a test tube which is fitted with a rubber stopper through which passes a viscometer 'B', and two other tubes. The bulb of the viscometer is filled with the solution in A by the application of suction. The suction to be exerted depends on the difference of water level in the aspirator 'E' and the jar placed underneath ; a water manometer 'M' attached to this reads the pressure applied for sucking the solution to the top of the bulb. All the adjustments are made by stop-cocks, well lubricated with good vacuum grease which facilitates an accurate adjustment of the pressure. It was found by working with saturated solutions that a pressure of 25 cm. was necessary for a decent interval of time.

The U-tubes 'C' and 'D' are connected with a three-way tap, T_2, which puts one or the other of the U-tube into communication with the dust-free air contained in the aspirator 'F'. The air from outside has to pass through the spiral 'S', coated inside with grease, which removes the dust particles suspended in the air which further comes into contact with spray fitted at the mouth of the aspirator F. Thus every precaution is taken to see that the air, coming into contact with the supersaturated solution, is free from dust, which, if present, will bring about crystallisation even in the "metastable" region.

It is necessary to pass a current of dust-free air through the whole apparatus several times before the commencement of each experiment. After closing the tap T_3, water is made to flow into the aspirator 'G'. The air in the upper part of the aspirator is forced out, and after being washed in the Woulfe's bottle 'H', is made to circulate through the whole apparatus and then finally ejected into the aspirator F. Purified air from the aspirator F passes into G when the water is removed from the bottom. Thus dust-free air is kept circulated through the apparatus from time to time.

When the solution is to be sucked up into the bulb of the viscometer, the tap T_2 is turned so as to put the U-tube D into communication with the air in the aspirator F, and suction applied by opening the tap T_1. When the bulb is to be emptied, tap T_1 is closed, and both the U-tubes are simultaneously put into communication with the air in the aspirator F. These two taps (T_1 and T_2) are fixed on the ground level very near the thermostat so that easy manipulation is ensured. Both the U-tubes contain a small quantity of water which replaces any loss due to evaporation of the solvent from the surface of the solution (a precaution necessary when dealing with supersaturated solutions).

The thermostat used was electrically heated and regulated by a toluene-mercury regulator. The temperature was measured by means of a thermometer reading up to 0.1°C.

In carrying out an experiment, the substance to be examined was weighed out carefully (the amount depending on its solubility) into a small conical flask and a measured quantity of water was added to make it saturated at the required temperature. The solubility data from the International Critical Tables (Vol. II, 1928) and Chemical Engineer's Hand-book (1950) were taken. The mouth of the flask was closed with a rubber stopper. The flask was heated in boiling water till all the solid had gone into solution. The solutions were always kept at least 5° above the temperature of saturation. The rubber stopper was then removed from the flask and the solution was carefully transferred to the bottom of the tube carrying the viscometer as quickly as possible. The rubber stopper was replaced and the whole apparatus was placed in the thermostat. After adjusting the viscometer in a vertical position, the solution was allowed to attain the constant temperature of the thermostat for about 30 minutes. The times taken for the ascent and descent of the solution were measured by means of a stop-watch reading 1/100 of a second, several readings having been taken for each temperature. The next reading was taken after cooling the thermostat, a degree or so below the original temperature. This process was repeated till a shower of crystals throughout the solution was noticed, as described by Miers and Issac (*loc. cit.*). Every time

a new experiment was started, the viscometer was cleaned and dried before use. From saturated solutions at different temperatures the viscosity at different temperature of supersaturation was noted.

FIG. 2

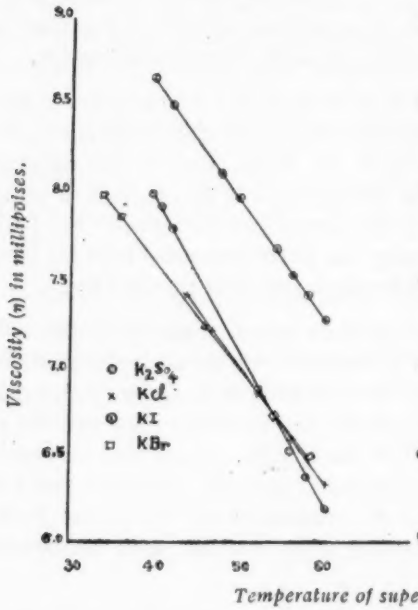
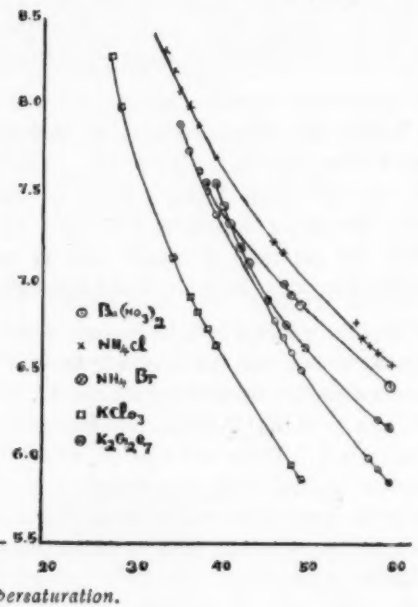


FIG. 3



Temperature of supersaturation.

The data are presented graphically in Figs. 2 and 3. It is seen that for substances like KCl, KBr, KI and K_2SO_4 (Fig. 2), temperature coefficient of solubility of which is constant throughout the ranges of temperature, the graph is a straight line; which shows that viscosity (η) varies linearly with temperature (T) of supersaturated solution for these substances. For other substances like $K_2Cr_2O_7$, $Ba(NO_3)_2$, NH_4Cl, NH_4Br and $KClO_3$, the straight line graph is not obtained (Fig. 3) ; their temperature coefficient of solubility is not also constant. η and T relation may be exponential in these cases.

The authors desire to express their thanks to Dr. B. S. Srikantan for the interest that he has been taking in this investigation.

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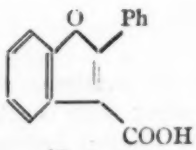
EXPERIMENTS ON THE SYNTHESES OF FURANO COMPOUNDS. PART VI. SELF-CONDENSATION OF *iso*COUMARANONE

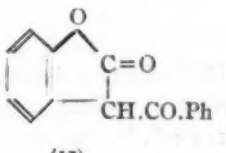
By J. N. Chatterjea

A synthesis of 2-phenylcoumarone-3-carboxylic acid is described. Self-condensation of *iso*coumaranone affords 3-*o*-hydroxyphenylacetylcoumaranone-2. It is shown that Pfeiffer and End.rs' 2-methylcoumarone-3-carboxylic acid is really 3-acetylcoumaranone-2. 3-Acetyl-, 3-propionyl- and 3-benzoyl-*iso*coumaranone can be prepared by the action of respective acid anhydride and the corresponding sodium salt on *iso*coumaranone.

In the synthesis* of 1 : 2 benzodiphenylene oxide, recently found in the coal tar distillation products by Kruber and Oberkobusch (*Chem. Ber.*, 1951, **84**, 831), 2-phenylcoumarone-3-carboxylic acid (I) was a suitable starting material. The present communication reports the synthesis of this acid. The exploration of alternative methods, as set forth below, has furnished interesting results.



(I)

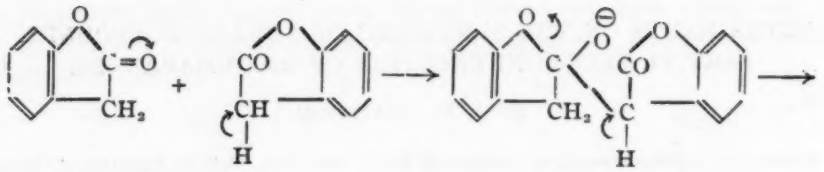


(II)

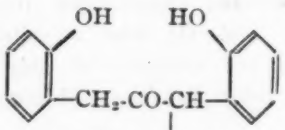
It was hoped that the isomeric compound 3-benzoylcoumaranone-2 (II), if synthetically available, would under appropriate conditions be transformed into the acid (I). A synthesis of (II) was attempted therefore by the action of ethyl benzoate on *iso*coumaranone. In the presence of metallic sodium, dry sodium ethoxide or better sodium hydride, a reaction took place yielding a product, $C_{16}H_{12}O_4$, and the ester was recovered unchanged. As the product is also formed if ethyl benzoate is omitted in the above experiments, its formation must be as a result of self-condensation (dimerisation) of *iso*coumaranone ($C_8H_6O_2$). This is particularly interesting as the self-condensation of coumaranone and its derivatives have been observed long ago and the constitution of the products elucidated (Fries and Pfaffendorf, *Ber.*, 1910, **43**, 212 ; 1911, **44**, 114 ; Baker and Banks, *J. Chem. Soc.*, 1939, 279).

The product is ketonic and acidic in character. It readily furnishes a copper chelate, $C_{32}H_{22}O_8Cu$, and shows a deep blue ferric reaction. With one mole of diazomethane, a monomethyl ether is obtained. This ether shows no ferric reaction and it is still a phenol as it affords an acetyl derivative. With acetic anhydride, the compound furnishes a diacetyl derivative. On these grounds, there is little doubt that the self-condensation product of *iso*coumaranone should be represented as (III). Ethyl α-γ-di(*o*-hydroxyphenyl)-acetoacetate (IV), obtained by the self-condensation of ethyl *o*-hydroxyphenylacetate in the presence of sodium ethoxide, was also found to have similar properties as (III). The probable mechanism of formation of (III) is as follows :

* The synthesis will be communicated later.

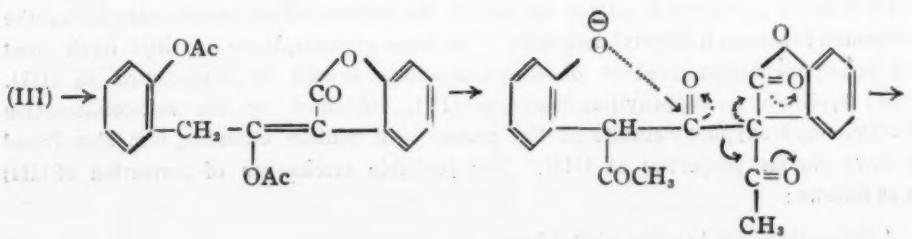


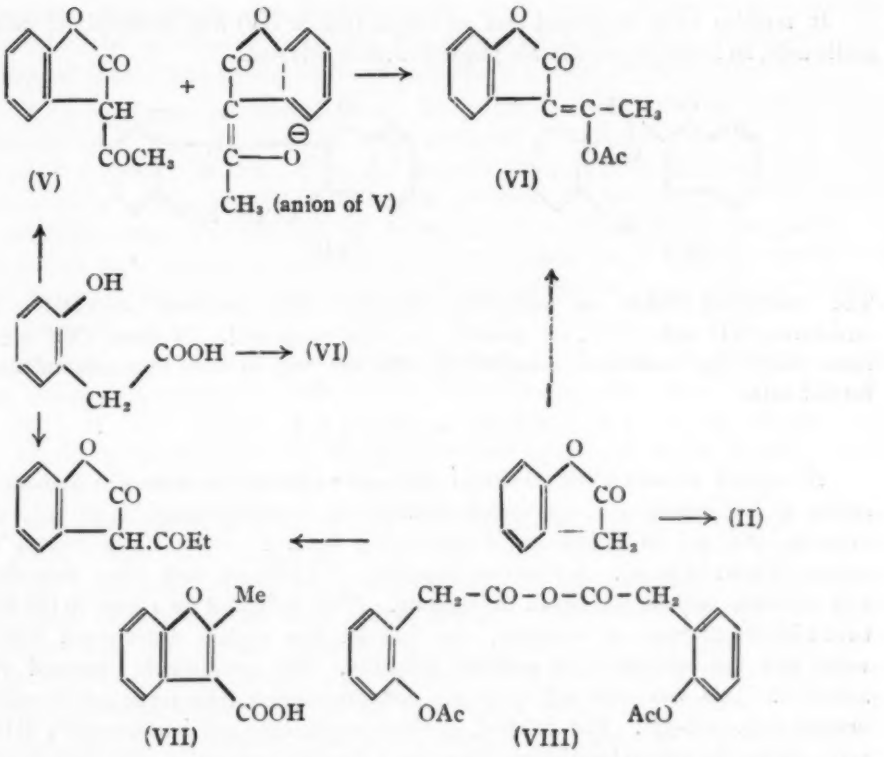
(III)



(IV)

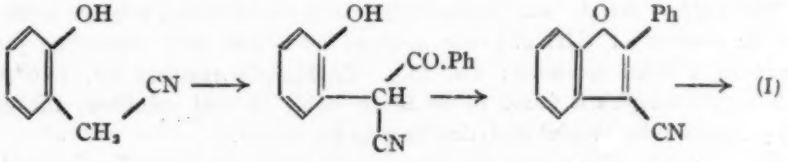
Although (III) affords a diacetyl derivative, as mentioned above, a deep-seated change takes place if sodium acetate is used along with acetic anhydride. This product, m.p. 119-20°, is also obtained from the diacetyl derivative by the further action of acetic anhydride and sodium acetate. The compound analysed as $C_{12}H_{10}O_4$ and contained one acetyl group. On hydrolysis, a compound, $C_{10}H_8O_3$, m.p. 135°, was obtained which behaved in a similar manner as (III). For example, the compound is acidic; it furnishes an oxime and a dinitrophenylhydrazone; it readily affords a copper chelate, and shows a deep blue ferric reaction. The compound $C_{10}H_8O_3$ must therefore be 3-acetylcoumaranone-2 (V). This was confirmed by the synthesis of its acetyl derivative (VI), m.p. 119-20°, from *iso*coumaranone, acetic anhydride and sodium acetate. It was soon discovered that a product of m.p. 135-36°, obtained by Pfeiffer and Enders (*Chem. Ber.*, 1951, **84**, 247) by the action of acetic anhydride on *o*-hydroxyphenylacetic acid in pyridine and alleged to be 2-methylcoumarone-3-carboxylic acid (VII), is identical with the compound, $C_{10}H_8O_3$, obtained above. Pfeiffer and Enders' product is therefore (V) and its methyl ester described by them is really the methyl ether (enol). The so-called anhydride (VIII), m.p. 118-19°, obtained by them by the action of acetic anhydride and sodium acetate on *o*-hydroxyphenylacetic acid, was identified as (VI).





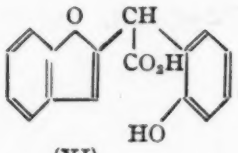
*iso*Coumaranone was also acylated with propionic anhydride and sodium propionate, yielding 3-propionylcoumaranone-2. 3-Benzoylcoumaranone-2 (II) was similarly prepared employing benzoic anhydride and sodium benzoate.

Although it has not yet been proved feasible to convert (II) into the acid (I), this was obtained in the following manner :

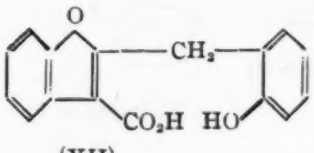


The keto-nitrile (IX), obtained from *o*-hydroxyphenylacetonitrile (Robertson *J. Chem. Soc.*, 1936, 420; Offe and Jatzkewitz, *Chem. Ber.*, 1947, **80**, 469) and ethyl benzoate, readily cyclised in the presence of acid into 3-cyano-2-phenylcoumarone (X). On mild alkaline hydrolysis (X) afforded the related amide; the acid (I) was, however, obtained along with benzoic acid under drastic conditions. The latter arises by the fission of the furan ring. The synthesis was confirmed by the decarboxylation of (I) to 2-phenylcoumarone.

It remains to be mentioned that on boiling (III) or (IV) with hydrochloric acid in acetic acid, an isomeric non-ketonic phenolic acid is obtained.



(XI)



(XII)

The compound affords an anhydride (lactone) with propionic anhydride. Two structures, (XI) and (XII), are possible for this compound. Of these (XI) appears more likely but a decision between the two can only be made after accumulation of further data.

EXPERIMENTAL *

Attempted Condensation of Ethyl Benzoate with iso*Coumaranone*: *Self-condensation of* iso*Coumaranone*.—A cooled mixture of *iso*coumaranone (0.54 g.), ethyl benzoate (0.7 g.) in anhydrous thiophene-free benzene (15 c.c.) was treated with sodium hydride (0.12 g.). A vigorous evolution of hydrogen took place immediately and colorless sodium salt began to separate. After refluxing for 1 hour on the water-bath with the exclusion of moisture, the mixture was cooled, decomposed with ice water and the alkaline layer acidified carefully. The gum which separated easily solidified. This was collected (0.52 g.) and crystallised from acetic acid in colorless needles, m.p. 156-57°. The product, 3-o-*hydroxyphenylacetylcoumaranone*-2 (III) is very soluble in sodium bicarbonate, develops a deep blue coloration with alcoholic ferric chloride and a deep violet-purple colour with sulphuric acid, gradually turning from light violet to bluish green. (Found: C, 71.5, 71.6, 71.6; H, 4.5, 4.6, 4.5. $C_{16}H_{12}O_4$ requires C, 71.6; H, 4.5 per cent).

The same product is obtained if ethyl benzoate is omitted in the above preparation and if metallic sodium, dry sodium ethoxide or sodium methoxide be employed.

The *copper chelate* was prepared by the action of copper sulphate to the aqueous alcoholic solution of (III) and was obtained as a dull grey crystalline precipitate. (Found in a dried specimen: Cu, 10.5. $C_{32}H_{22}O_8Cu$ requires Cu, 10.6 per cent). As the copper complex is found to be fairly stable in acid solutions, the compound (III) promises to be a useful analytical reagent for copper.

The *oxime* was prepared by adding hydroxylamine hydrochloride to a solution of the compound in sodium bicarbonate and leaving the mixture for 48 hours, followed by careful acidification with hydrochloric acid. It crystallised from dilute alcohol in colorless needles, m.p. 185-86° (decomp.). (Found: N, 5.0. $C_{16}H_{13}O_4N$ requires N, 5.0 per cent).

If the oxime is prepared in pyridine, it forms a compound with pyridine, crystallising from alcohol in colorless prisms, m.p. 155-56° (decomp.). (Found: C, 70.1; H, 5.3; N, 7.7, 7.7. $C_{16}H_{13}O_4N.C_5H_5N$ requires C, 69.6; H, 5.0; N, 7.7 per cent).

*All m.p.s are uncorrected.

The same compound is also obtained if the above mentioned oxime is crystallised from alcoholic pyridine. On heating the compound emits a smell of pyridine. The compound is soluble in sodium hydroxide and shows a bluish green ferric reaction.

With one mole of diazomethane, the enolic *monomethyl ether* was readily obtained from (III), crystallising from methanol in colorless needles, m.p. 134°. (Found: C, 71.9; H, 5.2. $C_{17}H_{14}O_4$ requires C, 72.3; H, 5.0 per cent). The compound is soluble in sodium hydroxide and shows no ferric reaction. The *acetate* of this enolic ether was obtained by boiling it with acetic anhydride for 2 hours. It crystallises from alcohol in colorless prisms or leaflets, m.p. 120-21°. (Found: C, 70.4, 70.5; H, 4.9, 5.2; COMe, 13.8. $C_{19}H_{16}O_5$ requires C, 70.4; H, 4.9; 1COMe, 13.2 per cent).

The *diacetate* of (III) was obtained by boiling with acetic anhydride for 2 hours. The compound crystallised from alcohol in colorless needles, m.p. 131°. (Found: C, 68.3; H, 4.7; COMe, 24.2. $C_{20}H_{16}O_6$ requires C, 68.2; H, 4.6; 2COMe, 24.4 per cent). It is insoluble in dilute alkali and shows no ferric reaction. With sulphuric acid it develops a similar colour reaction as (III).

Self-condensation of Ethyl o-Hydroxyphenylacetate (cf. McElvain and Roberts, *J. Amer. Chem. Soc.*, 1937, **59**, 2007).—The ester (3.6 g., prepared according to Offe and Jatzkewitz, *loc. cit.*) in dry benzene (15 c.c.) was refluxed for 6 hours with anhydrous sodium ethoxide from sodium (1.0 g.). The mixture was decomposed with ice water and the product isolated from the aqueous layer as usual. *Ethyl αγ-di-(o-hydroxyphenyl)-acetoacetate* (IV) crystallised from acetic acid or benzene in colorless prismatic needles, m.p. 147-48° [mixed m.p. with (III) was 140°]. (Found: C, 68.3; H, 5.7. $C_{18}H_{16}O_5$ requires C, 68.9; H, 5.7 per cent). The compound is soluble in sodium bicarbonate, affords a copper chelate and shows a deep blue ferric reaction. With sulphuric acid a similar colour reaction as (III) is given.

The self-condensation could not be brought about by *iso*propylmagnesium bromide which was reported to be particularly successful with ethyl phenylacetate (Conant and Blatt, *J. Amer. Chem. Soc.*, 1929, **51**, 1227).

Action of Acetic Anhydride and Sodium Acetate on 3-o-Hydroxyphenylacetylcoumaranone-2 (III).—The compound (1.0 g.) was boiled for 1½ hours with acetic anhydride (10 c.c.) and sodium acetate (fused, 1.0 g.). The *product* (VI) (0.65 g.) crystallised from alcohol in pinkish mica-like plates, m.p. 119-20° which developed a bluish coloration with sulphuric acid. (Found: C, 66.0, 66.2; H, 4.6, 4.7; COMe, 21.0. $C_{12}H_{10}O_4$ requires C, 66.0; H, 4.6; 1COMe, 19.7 per cent). (Pfeiffer and Enders, *loc. cit.*, report C, 65.16, 64.96; H, 4.88, 4.62 for the same compound, m.p. 118-19°; mixed m.p. 119-20°).

Hydrolysis of the Product.—The acetyl compound (0.5 g.) was dissolved in acetic acid (5 c.c.) and refluxed with concentrated hydrochloric acid (0.5 c.c.) for ½ hour. On dilution with water colorless leaflets of *3-acetylcoumaranone-2* appeared, crystallising from dilute alcohol in colorless needles, m.p. 135°, undepressed on admixture with Pfeiffer and Enders' so-called 2-methylcoumarone-3-carboxylic acid, m.p. 135-36°. The compound is volatile in steam and develops a deep blue ferric reaction.

With sulphuric acid it produces a blue colour and readily affords a copper chelate with copper sulphate. (Found: C, 68.1; H, 4.6. $C_{10}H_8O_3$ requires C, 68.3; H, 4.6 per cent). The *oxime*, prepared in sodium bicarbonate solution, crystallised from dilute alcohol in colorless leaflets, m.p. 156° (decomp.)*. (Found: N, 6.9 $C_{10}H_9O_3N$ requires N, 7.3 per cent). The 2:4-*dinitrophenylhydrazone* crystallised from a large volume of acetic acid in orange-red plates, m.p. 238° (decomp.). (Found: N, 15.2. $C_{16}H_{12}O_6N_4$ requires N, 15.7 per cent).

Action of Acetic Anhydride and Sodium Acetate on iso*Coumaranone.*—*iso*-Coumaranone (1.0 g.) was boiled with acetic anhydride (10 c.c.) and sodium acetate (0.5 g.) for ½ hour. The product (VI) crystallised from alcohol in pinkish plates, m.p. 119-20°, identical with the product mentioned above; yield 0.65 g.

3-*Propionylcoumaranone*-2: (*a*) *From* o-*Hydroxyphenylacetic Acid.*—A solution of *o*-hydroxyphenylacetic acid (3.0 g.) and propionic anhydride (7.8 c.c.) in pyridine (40 c.c.) was heated on the water-bath for 4 hours. The mixture was cooled, acidified with concentrated hydrochloric acid and the crystalline matter that separated was collected after 24 hours. The product was dissolved in sodium bicarbonate, clarified by norit and acidified. Bluish white crystals of 3-*propionylcoumaranone*-2 (0.5 g.) appeared, crystallising from dilute methanol in bluish leaflets, m.p. 98-99°. (Found: C, 69.6; H, 5.3. $C_{11}H_{10}O_3$ requires C, 69.5; H, 5.3 per cent). The compound shows a deep blue ferric reaction and affords a copper chelate with copper sulphate. The enolic *methyl ether* was prepared by diazomethane and crystallised from dilute methanol in colorless needles, m.p. 101°, showing no ferric reaction. (Found: C, 70.7; H, 6.0. $C_{12}H_{12}O_3$ requires C, 70.6; H, 6.0 per cent).

(*b*) *From* iso*Coumaranone.*—This was done by boiling *iso*coumaranone (0.5 g.) with propionic anhydride (5 c.c.) and sodium propionate (0.3 g.). The gummy product obtained by addition of water was extracted with sodium bicarbonate, filtered and acidified to provide a poor yield of the propionyl derivative, m.p. and mixed m.p. 99°.

3-*Benzoylcoumaranone*-2 (II).—A mixture of *iso*coumaranone (1.0 g.); benzoic anhydride (5 g.) and dry sodium benzoate (1.2 g.) was heated for 3 hours in vacuum at 170°-180° (cf. Allan and Robinson, *J. Chem. Soc.*, 1924, **125**, 2192). The semi-solid mass was taken up in benzene and shaken for ½ hour with a solution of sodium carbonate (80 c.c., 10%). The aqueous layer was clarified with norit and acidified. Benzoic acid mixed with a bluish green mass appeared. The mixture was collected and then warmed with water (150 c.c.) till benzoic acid dissolved, leaving an oil. The mixture was cooled under the tap till the oil solidified and then collected quickly. 3-*Benzoylcoumaranone*-2 (II) was obtained as greenish lumps (0.6 g.), crystallising from aqueous alcohol in greenish leaflets, m.p. 100°. On sublimation this was obtained in cream-coloured needles, m.p. 100°. The compound is soluble in bicarbonates and gives a deep blue ferric reaction. It readily affords a copper chelate and with sulphuric acid produces a yellowish green solution rapidly, changing from green to blue. (Found: C, 76.0; H, 4.6. $C_{15}H_{10}O_3$ requires C, 75.6; H, 4.2 per cent). The enolic *methyl ether* crystallised from aqueous methanol in colorless prisms, m.p. 108°. (Found: C, 75.8; H, 4.9. $C_{16}H_{12}O_3$ requires C, 76.2; H, 4.7 per cent).

* On keeping, the sample decomposed completely.

2-Phenylcoumarone-3-carboxylic Acid (I).—A mixture of *o*-hydroxyphenylacetonitrile (0.7 g.) (Robertson, *loc. cit.*) and ethyl benzoate (0.8 g.) in thiophene-free benzene (12 c.c.) was added to dry sodium ethoxide (from sodium, 0.24 g.), refluxed for 6 hours and left overnight. On working up the *keto-nitrile* (IX) was isolated (0.4 g.), crystallising in colorless prisms from ethyl acetate-light petroleum, m.p. 160-66° (with previous sintering due to cyclisation). (Found: N, 5.6. $C_{15}H_{11}O_2N$ requires N, 5.9 per cent).

Cyclisation.—The foregoing keto-nitrile (8.0 g.) was dissolved in acetic acid (20 c.c.) and boiled for 1 minute with HCl (conc., 4 c.c.). The whole mixture was basified and *3-cyano-2-phenylcoumarone* (X) was crystallised from dilute acetic acid in colorless plates, m.p. 80-82°, yield 6.5 g. (Found: C, 82.2; H, 4.4; N, 6.4. $C_{15}H_9ON$ requires C, 82.2; H, 4.2; N, 6.4 per cent).

Hydrolysis.—The nitrile (0.4 g.) was boiled for 4 hours with aqueous alcoholic potash (10 c.c., 10%). Very soon colorless silky needles of the *amide* (X, $CONH_2$ in place of CN) appeared which resisted further hydrolysis due to its low solubility in alcohol. Crystallised from acetic acid, this was obtained in colorless needles, m.p. 261°. The compound can be purified by sublimation. (Found: N, 5.9. $C_{15}H_{11}O_2N$ requires N, 5.9 per cent).

If the hydrolysis is done in diethyleneglycol for 7 hours at 160°-170°, the nitrile (3.8 g.) afforded a mixture of acids which on fractional crystallisation from dilute alcohol furnished *2-phenylcoumarone-3-carboxylic acid* (1.2 g.) in colorless needles, m.p. 192-94°. (Found: C, 75.2; H, 4.0. $C_{15}H_{10}O_3$ requires C, 75.5; H, 4.2 per cent). Benzoic acid (2.0 g.) was obtained from the filtrate. The *methyl ester* obtained by the action of diazomethane crystallised in prismatic needles from light petroleum, m.p. 80°. (Found: C, 75.8; H, 5.0. $C_{16}H_{12}O_3$ requires C, 76.2; H, 4.7 per cent). Decarboxylation of the acid by heating with 5 times the weight with lime afforded 2-phenylcoumarone as a colorless oil which quickly solidified. This crystallised from alcohol in colorless plates, m.p. 120-21° (lit. m.p. 120°) developing with sulphuric acid a greenish yellow solution, rapidly turning green. (Found: C, 86.4; H, 5.2. Calc. for $C_{14}H_{10}O$: C, 86.6; H, 5.2 per cent).

3-Acetyl-2-phenylcoumarone.—An excess of methylmagnesium iodide was added to the nitrile (X) and the mixture refluxed for 1½ hours. The dirty green complex on decomposition provided the ketone as an oil which did not solidify due to impurities. The *2:4-dinitrophenylhydrazone* crystallised from acetic acid in shining red plates, m.p. 210°. (Found: N, 13.2. $C_{22}H_{16}O_5N_4$ requires N, 13.5 per cent).

Action of Hydrochloric Acid on (III): *Isomerisation.*—The compound (III) (3.0 g.) was dissolved in acetic acid (40 c.c.) and boiled with HCl (conc., 10 c.c.) for 1½ hours. Water was added just to the crystallisation point and the *product* (2.4 g.) collected and crystallised from dilute acetic acid. This was obtained in colorless prisms, m.p. 194-95°, showing no ferric reaction. (Found: C, 71.6; H, 4.6. $C_{15}H_{12}O_4$ requires C, 71.6; H, 4.5 per cent). The compound dissolves in sulphuric acid imparting a stable violet colour. If crystallised from dilute pyridine, the compound forms a complex with pyridine, m.p. 125-28°. (Found: C, 72.6; H, 4.9; N, 4.3. $C_{16}H_{12}O_4$. C_5H_5N requires C, 72.7; H, 4.9; N, 4.0 per cent).

The crystals lose pyridine in the course of 2 months and fall to powder and the m.p. rises to 194-95°. The *methyl ester* crystallises from dilute methanol in colorless needles, m.p. 131°. (Found: C, 72.0; H, 5.0. $C_{17}H_{14}O_4$ requires C, 72.3; H, 5.0 per cent). The *acetyl* derivative, prepared with acetic anhydride and sodium acetate, crystallises from acetic acid in colorless needles, m.p. 220°. (Found: C, 69.4; H, 4.6; -$COMe_3$, 13.9. $C_{18}H_{14}O_5$ requires C, 69.6; H, 4.5; 1COMe, 14.0 per cent). The *propionyl* derivative was prepared with propionic anhydride and a trace of pyridine. It crystallised from alcohol in colorless prisms, m.p. 170°. (Found: C, 70.2; H, 5.0. $C_{19}H_{16}O_5$ requires C, 70.4; H, 5.0 per cent). If pyridine is not added the sole product is an *anhydride* (lactone), crystallising from alcohol in thick plates, m.p. 138-39°. (Found: C, 77.2; H, 4.3. $C_{16}H_{10}O_3$ requires C, 76.8; H, 4.0 per cent). The compound is insoluble in dilute alkali.

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SYNTHESIS OF CYANINE DYES BY THE CONDENSATION OF *p*-DIALKYLAMINOBENZALDEHYDE WITH APPROPRIATE HETEROCYCLIC COMPOUNDS. PART VI

By M. Q. Doja and Arun Kumar Sinha

p-Dimethylamino- and *p*-diethylamino-benzaldehydes have been condensed with 6-chloro-, 6-bromo-, 6-iodo-quinaldine ethiodide and 6-formamido- and 6-acetamido-quinaldine ethiodide respectively. The effect on sensitisation of substitution in the quinaldine nuclei of *p*-diethylamino- and *p*-dimethylamino-cyanines has been studied. The optical, chemical, dyeing and photographic properties of these compounds have been examined and a few intermediates have been described.

Earlier workers have prepared cyanines from a variety of heterocyclic compounds containing reactive methyl groups. The fact that the styryl dyes are powerful photographic sensitisers was pointed out by Mills and Pope (*J. Chem. Soc.*, 1922, **121**, 946), who showed that the reaction, which proceeded smoothly in absolute alcohol with piperidine as a catalyst, was a general one. It is of interest therefore to investigate the nature of new cyanines produced in this manner by suitable substitutions, which latter are known to affect the sensitising power of the dyes. The present investigation was undertaken with this object.

Three new dyes have been prepared by introducing the chloro, bromo and iodo group respectively in the 6-position of 2-*p*-dimethylaminostyrylquinoline ethiodide and two more by introducing the formamido and acetamido group in the same position in 2-*p*-diethylaminostyrylquinoline ethiodide.

The dyes have all been recrystallised from methyl alcohol and obtained as well-formed pleochroic crystals, possessing various degrees of reflex. They are slightly soluble in cold water excepting the formamido and acetamido dyes, which dissolve only on prolonged heating. The rectified spirit solutions of the dyes are violet-red. The chief characteristics of the dyes are recorded in Table I. The relative resistances to decolorisation by $N/100$-HCl to 2 c.c. of 1/100,000 solutions of the different dyes in rectified spirit have been determined by titration and the comparative intensities of these solutions computed colorimetrically. Dimethylamino dyes have been found more resistant to decolorisation than the corresponding diethylamino compounds.

The dyes produced shades of varying colour on cotton, silk and wool, when dyed from alcoholic baths, as shown in Table II; but the shades were fugitive to sunlight and not fast to washing.

The yields of chloro, bromo and iodo dyes in the respective cases are 53·7%, 49.1% and 28.2%. This is difficult to explain, but the observations of Bennet *et al.* (*J. Chem. Soc.*, 1935, 1827; 1937, 1112) that among the halogens, iodine, the largest atom, controls its valence electrons less powerfully and the magnitude of the effect on neutralisation by electron relay is of the order $I > Br > Cl$, may have

something to do with it. It is noteworthy that the m.p.'s of the dimethylamino dyes are greater than those of the their diethyl analogues (cf. Doja and Banerjee, this *Journal*, 1946, **23**, 222).

An interesting observation is that the acetic acid solutions of these dyes (with the exception of the chloro and the bromo derivatives) deepen in colour on warming. When the solutions are cooled, the intensity diminishes and the original colour is slowly regained. The formamido dye produces brownish yellow coloration on cooling and brownish red on warming. The effect is more pronounced in aqueous-acetic acid solution. This phenomenon has been previously reported in the case of cyanines derived from thiazoles (Doja and Banerjee, *loc. cit.*, p. 217).

The fluorescence of weak alcoholic solutions (1 : 100,000) of these dyes is shown in Table III (cf. Doja, *ibid.*, 1940, **17**, 348).

The sensitisation and absorption spectra of these dyes are shown in Fig. 1. None of the halogen derivatives of these dyes are good sensitisers. The introduction of the chloro, bromo and iodo group in the 6-position of 2-*p*-dimethylaminostyryl-quinoline ethiodide depresses the sensitization as compared to 2-*p*-diethyl analogues. The formamido (E) and acetamido (F) dyes are remarkably good sensitisers, sensitizing up to 6900Å and 6800Å.

These somewhat unusual sensitising effects may be attributable to the association of the dye (Sheppard, *Rev. Mod. Phys.*, 1942, **14** 303; Scheibe, *Z. angew. Chem.*, 1936, **49**, 563; 1937, **50**, 51; Jelly, *Nature*, 1936, **138**, 1009; 1937, **139**, 631; Leermaker, *J. Chem. Phys.*, 1937, **5**, 878; Dickinson, *Phot. J.*, 1948, **88B**, 97; *Trans. Faraday Soc.*, 1947, **43**, 486), its compactness (Brooker *et al.*, *J. Phot. Sci.*, 1953, **1**, 173) and its planar configuration (West and Carrol, *J. Chem. Phys.*, 1951, **19**, 417), which individually or collectively are known to be important factors affecting the absorption and sensitisation of the dye.

EXPERIMENTAL

2-p-*Dimethylaminostyryl-6-chloroquinoline Ethiodide.*—6-Chloroquinaldine ethiodide (0.33 g.), *p*-dimethylaminobenzaldehyde (0.15 g.), absolute alcohol (15 c.c.) and piperidine (3 drops) were refluxed for 30 minutes on a small flame. The dye began to separate during the later period of heating and a further amount separated on cooling, yield 0.25 g. (53.7%). It was recrystallised from methyl alcohol, m.p. 266-67°. (Found : N, 6.13 ; Cl + I, 35.1. $C_{21}H_{22}N_2$ Cl I requires N, 6.0 ; Cl + I, 34.94 per cent).

2-p-*Dimethylaminostyryl-6-bromoquinoline Ethiodide.*—On boiling under reflux and a moisture-absorbing $CaCl_2$ tube, an absolute alcoholic solution (20.0 c.c.) of 6-bromoquinaldine ethiodide (0.76 g.), *p*-dimethylaminobenzaldehyde (0.30 g.) and two drops of piperidine, an intense magenta colour developed. The refluxing was continued for 45 minutes. The dye was obtained from the cold solution, yield 0.5 g. (49.1%); it was then recrystallised from methyl alcohol, m.p. 264°. (Found : N, 5.5 ; Br + I, 40.9. $C_{21}H_{22}N_2$ BrI requires N, 5.5 ; Br + I, 40.66 per cent).

FIG. 1

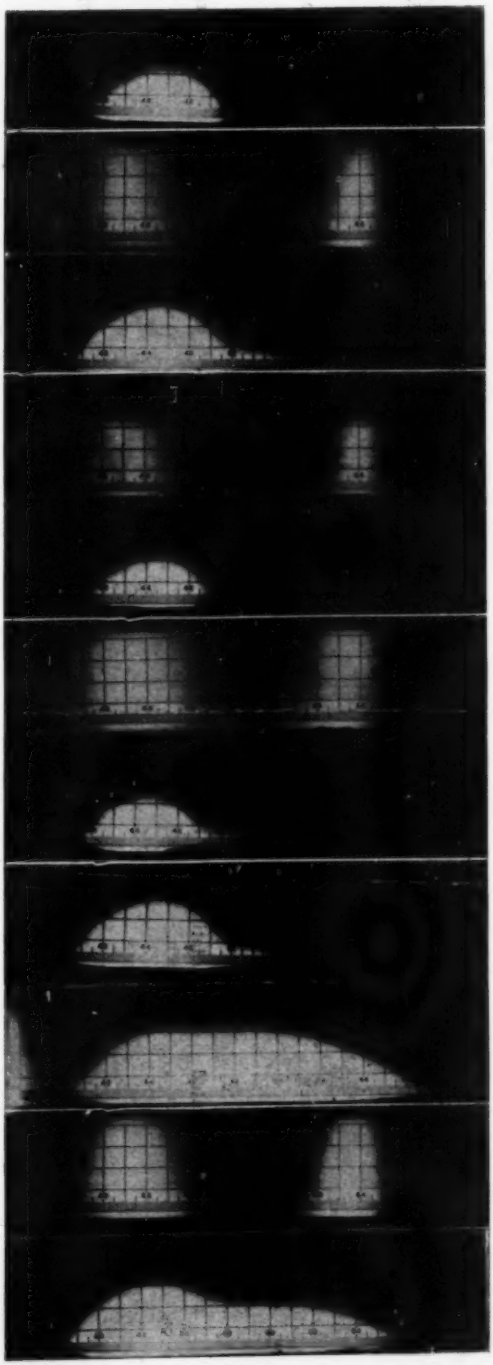
Unbathed
Absorption
B1
Sensitisation
Absorption
C1
Sensitisation
Absorption
D1
Sensitisation
Absorption
E
Sensitisation
Absorption
F
Sensitisation

TABLE I

Compound.	Colour and shape of crystals.	Reflex.	Pleochroism. Colour of light in one position of polariser.	Pleochroism. Colour after rotation through 90°.	Relative intensity of colour	$N/100$ HCl required.	Relative resistance to decolorisation.	Extra sensitisation. Total range of sensitization in Å.	Extra sensitisation. Maximum in Å.	Frequency of maximum absorption $\times 10^{10}$ Å.
B_1	Dark grey felted clusters	Weak greenish white.	Weak green.	Glass like	3.49	45.10 c.c	21.5	5200-6250	Uniform sensitization. No maximum.	55555
C_1	Dirty mauve powder.	Pinkish white.	Colorless.	Pink.	4.04	44.35	21.1	Nil	No extra-sensitization.	55555
D_1	Magenta-grey crystals.	White.	Dirty yellow.	Weak rose.	1.00	44.00	21.0	5100-6100	Faint maximum at 6000	55046
E	Green stunted needles	Scintillating green.	Bottle green.	Greenish yellow.	2.92	24.00	11.4	5200-6900	Uniform, no maximum.	57143
F	Sage-green shining platelets.	Strong yellowish green.	Light yellow.	Dirty white.	4.42	2.10	1.0	5100-6800	Faint maximum at 5600	56075

B_1-2-*p*-Dimethylaminostyryl-6-chloroquinoline ethiodide.

C_1-2-*p*-Dimethylaminostyryl-6-bromoquinoline ethiodide.

D_1-2-*p*- „ „ -6-iodo- „ „

E-2-*p*-Diethyl „ -6-formamido „ „

F-2-*p*-Diethyl „ -6-acetamido „ „

F-2-*p*-Diethyl ,, -6-acetamido ,, ,,

5—1914P—3

TABLE II

* Compound	B_1	C_1	D_1	E	F
Silk	Weak reddish violet	Reddish violet	Pink	Pink	Indigo blue
Wool	Reddish violet	Deep reddish violet	Pink	Weak rose red	Reddish violet
Cotton	Reddish violet	Reddish violet	Light reddish violet	Violet-red	Indigo blue

* Refers to same numbering and nomenclature as in Table I.

TABLE III

Colour of the fluorescent beam seen at right angles to the incident beam.

Wallace colour filter Number.	B_1.	C_1.	D_1.	E.	F.
1	Deep red.	Light absorbed.	Brilliant red.	Light absorbed.	Deep red.
2	Yellowish red.	Brilliant red.	Red.	Flaming red.	Crimson.
3	Reddish violet.	Violet (with reddish tinge)	Reddish violet.	Rose-red.	Deep pink.
4	Yellowish red.	Bright orange-red.	Flaming red.	Orange-red.	Yellowish red.
5	Greenish yellow.	Orange-yellow.	Yellow	Yellow with greenish tinge.	Lemon-yellow
6	Yellow.	Light yellow.	Light absorbed.	Lemon-yellow.	Greenish yellow
7	Light green.	Sage-green.	Emerald-green.	Yellowish green.	Green
8	Bluish green.	Bluish green.	Bluish green.	Bluish green.	Bluish green
9	Blue-violet.	Blue.	Sapphire-blue.	Blue.	Violet-blue
10	Light absorbed.	Weak yellow.	Light yellow.	Lemon-yellow.	Light absorbed.

2-p-*Dimethylaminostyryl-6-iodoquinoline Ethiodide*.—6-Iodoquinaldine ethiodide (0.4 g.), *p*-dimethylaminobenzaldehyde (0.15 g.), absolute alcohol (20 c.c.) and piperidine (4 drops) were boiled under reflux for 45 minutes. The dye began to separate even while the solution was boiling. On cooling, the dye separated as wooly clusters, yield 0.15 g. (28.2%). When purified with methyl alcohol, the dye had m.p. 271-72°. (Found: N, 4.9; I, 45.8. $C_{21}H_{22}N_2I_2$ requires N, 5.03; I, 45.6 per cent).

6-Formamidoquinaldine has been described by Browning, Cohen, Ellingworth, and Gulbransen. *Proc. Roy. Soc.*, London, 1924, **96B**, 317) and m.p. recorded, 131-32°. This compound has now been prepared by the method similar to Barger and Robinson for the preparation of 3-formamidoquinaldine (*J. Chem. Soc.*, 1929, 2947). 6-Aminoquinaldine (2.1 g.) and formic acid (12.0 g.) were refluxed together for 3 hours. The liquid was then poured into water, sodium carbonate was added till alkaline, when an oily product floated on the surface and solidified after 24 to 48 hours. It was recrystallised from xylene, m.p. 133-34°, yield 1.0 g. (Found: N, 14.9. Calc. for $C_{11}H_{10}ON_2$: N, 15.0 per cent).

6-Formamidoquinaldine ethiodide was prepared by refluxing 6-formamidoquinaldine (1.0 g.) and ethyl iodide (0.5 c.c.) in nitrobenzene (5.0 c.c.) for 4 hours on the water-bath and then cooling. It was recrystallised from aqueous alcohol, yield 0.3 g., m.p. 240-43° (blackening from 237°). (Found: I, 36.6. $C_{13}H_{15}ON_2I$ requires I, 37.1 per cent).

2-p-*Diethylaminostyryl-6-formamidoquinoline ethiodide* was obtained by refluxing 6-formamidoquinaldine ethiodide (0.34 g.), *p*-diethylaminobenzaldehyde (0.18 g.), absolute alcohol (15 c.c.) and piperidine (3 drops) for 6 hours. The solution was then concentrated to 6 c.c. and on cooling, crystals deposited, yield 0.12 g. (23.7%). The dye was recrystallised from methyl alcohol, m.p. 225-26°. (Found: N, 8.5; I, 25.4. $C_{24}H_{28}ON_3I$ requires N, 8.38; I, 25.3 per cent).

6-Acetamidoquinaldine ethiodide was prepared according to the method of Wilson (*J. Chem. Soc.*, 1938, 556).

2-p-*Diethylaminostyryl-6-acetamidoquinoline ethiodide* was obtained by refluxing, under a moisture trap, a mixture of 6-acetamidoquinaldine ethiodide (0.45 g.) and *p*-diethylaminobenzaldehyde (0.22 g.) in absolute alcohol (15 c.c.) with piperidine (2 drops) for 1½ hours, when the dye separated, yield 0.3 g. When recrystallised from methyl alchohol, the dye came down in rectangular plates, m.p. 251-52°. (Found: N, 7.95; I, 24.4. $C_{25}H_{30}ON_3I$ requires N, 8.1; I, 24.66 per cent).

Thanks are due to Prof. L. M. Chatterjee, Head of the Department of Physics, Science College, Patna for help in taking the absorption spectra.

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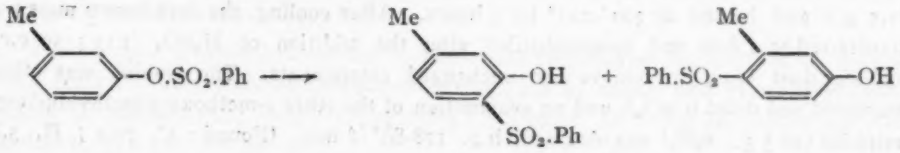
FRIES REARRANGEMENT OF *m*-TOLYL ARYLSULPHONATES

By Miss A. A. Aleykutty and V. Baliah

m-Tolyl benzenesulphonate, *p*-toluenesulphonate and *o*-toluenesulphonate undergo the Fries rearrangement when heated with anhydrous aluminium chloride to furnish in each case a mixture of *o*- and *p*-hydroxy-sulphones. The structures of all the sulphones, thus obtained, have been established by synthesising them unequivocally.

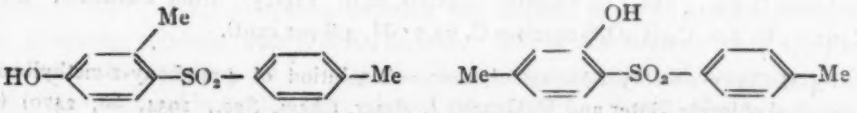
In continuation of our previous work (*Curr. Sci.*, 1953, **22**, 307; this *Journal*, 1954, **31**, 513) on the Fries rearrangement of arylsulphonates, the present paper deals with the rearrangement of *m*-tolyl arylsulphonates. The rearrangement, as in previous cases, did not occur to any appreciable extent below 100°. The temperature range of 130°-140° was found to be the most suitable, as charring occurred at higher temperatures.

The rearrangement of each of the arylsulphonates used in the present work resulted in the formation of both the *o*- and *p*-hydroxy-sulphones. *m*-Tolyl benzenesulphonate (I) yielded a mixture of 2-hydroxy-4- and 4-hydroxy-2-methyldiphenylsulphones (II and III). As a rule, the *o*-hydroxysulphone is more soluble in non-hydroxylic solvents than the *p*-isomer. This difference in solubility proved helpful in effecting their separation. The identity of the sulphones was established by their unambiguous synthesis.



(I) (II) (III)

The Fries rearrangement of *m*-tolyl *p*-toluenesulphonate was recently studied by Amin *et al.* (*J. Sci. Ind. Res.*, 1954, **13B**, 182) and they reported the formation of only one isomer. They characterised this compound as 4-hydroxy-2:4′-dimethyldiphenylsulphone (IV) without furnishing any evidence. The present work has revealed that their compound is actually 2-hydroxy-4:4′-dimethyldiphenylsulphone (V). Amin *et al.* reported the melting points of their sulphone and its methyl ether as 144° and 132° respectively. 2-Hydroxy-4:4′-dimethyldiphenylsulphone and its methyl ether, which have been synthesised unequivocally, are found to melt at 145-47° and 131-32° respectively.



(IV) (V)

EXPERIMENTAL

Fries Rearrangement of m-*Tolyl Benzenesulphonate.*—An intimate mixture of *m*-tolyl benzenesulphonate (49.6 g.) and powdered anhydrous aluminium chloride (40 g.) was heated to 130° and kept at 130°-140° for 45 minutes. After cooling, it was decomposed with dilute HCl and ice. The oily substance separating was ether-extracted. The ethereal solution was then thoroughly extracted with a 10% NaOH solution. Acidification of the alkali extract furnished a product (11.6 g., 23%) which was found to be a mixture of 2-*hydroxy*-4- and 4-*hydroxy*-2-*methyldiphenylsulphones*. It was boiled four times with CCl_4 (30 c.c. each). The insoluble component was obtained as an oil. The CCl_4 extract on evaporation to dryness yielded 8.8 g. (18% based on the sulphonate used) of a substance which, on crystallisation from ethanol, melted at 124-25°, unchanged in mixture with the synthetic sample of 2-hydroxy-4-methyldiphenylsulphone (*vide infra*). (Found: C, 62.8; H, 4.7. $C_{13}H_{12}O_3S$ requires C, 62.9; H, 4.8 per cent). The CCl_4-insoluble portion (2.5 g., 5%) solidified gradually on keeping aside for a week. It crystallised from benzene in plates, m.p. 119-21°, mixed m.p. with an authentic sample of 4-hydroxy-2-methyldiphenylsulphone was undepressed. (Found: C, 62.6; H, 5.1. Calc. for $C_{13}H_{12}O_3S$: C, 62.9; H, 4.8 per cent).

2-*Methoxy*-4-*methyldiphenyl Sulphide.*—To a solution of sodium ethoxide (2.3 g. of sodium in 30 c.c. of absolute ethanol) thiophenol (11 g.) was added and evaporated to dryness. The resulting sodium thiophenate was mixed with 2-iodo-5-methylanisole (Li and Adams, *J. Amer. Chem. Soc.*, 1935, **57**, 1565) (24.9 g.) and copper powder (2.5 g.) and heated at 200°-220° for 3 hours. After cooling, the dark brown mass was transferred to a flask and steam-distilled after the addition of H_2SO_4 (1:1; 50 c.c.) and zinc dust (10 g.) to remove any unchanged components. The residue was ether-extracted and dried ($CaCl_2$), and on evaporation of the ether 2-methoxy-4-methyldiphenyl sulphide (20.5 g., 89%) was obtained, b.p. 178-80°/8 mm. (Found: C, 73.1; H, 5.8. $C_{14}H_{14}OS$ requires C, 73.0; H, 6.1 per cent).

2-*Methoxy*-4-*methyldiphenylsulphone.*—A solution of the above sulphide (4.6 g.) in hot glacial acetic acid was treated with excess of a 10% solution of $KMnO_4$ and kept aside for 20 minutes. The solution was then decolorised with SO_2. The *sulphone* which separated out (4.6 g., 88%) was crystallised from methanol as clusters of long needles, m.p. 155-56°. (Found: C, 63.6; H, 5.3. $C_{14}H_{14}O_3S$ requires C, 64.1; H, 5.3 per cent).

2-*Hydroxy*-4-*methyldiphenylsulphone.*—A mixture of the above sulphone (2.6 g.) and HI (*d* 1.7, 8 c.c.) was heated at 200° for 2½ hours, cooled and then poured into water. The solid obtained was filtered off, washed with water and extracted with a 10% solution of NaOH. Acidification of the alkali-extract furnished the *hydroxysulphone* (2.1 g., 85%) in rhombic crystals, m.p. 124-25°, from methanol. (Found: C, 62.5; H, 4.9. $C_{13}H_{12}O_3S$ requires C, 62.9; H, 4.8 per cent).

4-*Methoxy*-2-*methyldiphenylsulphone.*—A solution of 4-methoxy-2-methylbenzenesulphonyl chloride (Suter and McKenzie, *J. Amer. Chem. Soc.*, 1934, **56**, 2470) (11 g.) in CS_2 (30 c.c.) was mixed with $AlCl_3$ (anhyd., 10 g.). Pure benzene (3.9 g.) was added

slowly and refluxed for 1½ hours on a water-bath. It was then treated with HCl and crushed ice, and CS_2 removed. The resulting pasty mass (11 g., 84%) was washed with a few c.c. of methanol. It crystallised from benzene as needles, m.p. 92-93°. The same sulphone was obtained in 80% yield by the Friedel-Crafts reaction of benzenesulphonyl chloride with 3-methoxytoluene in CS_2. (Found: C, 64.5; H, 5.4. $C_{14}H_{14}O_3S$ requires C, 64.1; H, 5.3 per cent).

4-Hydroxy-2-methyldiphenylsulphone was obtained in 85% yield by demethylation of the above sulphone with HI in the usual way. It solidified slowly. Crystallisation from benzene gave plates, m.p. 118-20°. (Found: C, 62.5; H, 4.5. Calc for $C_{13}H_{12}O_3S$: C, 62.9; H, 4.8 per cent). Vorozhtsov and Kuchkarov (*J. Gen. Chem.*, 1949, **19**, 1943), who prepared it by the reaction of benzenesulphonic acid with *m*-cresol, reported m.p. 120°.

Fries Rearrangement of m-*Tolyl* p-*Toluenesulphonate.*— The rearrangement of this sulphonate, when carried out at 140°-150° as before, afforded a mixture of *2-hydroxy-4:4'-* and *4-hydroxy-2:4'-dimethyldiphenylsulphones.* The yield was 35%. The separation of the two isomers was effected by taking advantage of the greater solubility of the 2-hydroxysulphone in benzene. The fraction which was sparingly soluble in benzene, after several recrystallisations from toluene, gave the 4-hydroxysulphone, m.p. 151-52°. (Found: C, 64.0; H, 5.5. $C_{14}H_{14}O_3S$ requires C, 64.1; H, 5.3 per cent). The fraction which was easily soluble in benzene, after repeated crystallisation from ethanol, gave the 2-hydroxysulphone, m.p. 145-47°. (Found: C, 64.2; H, 5.1 per-cent). The identity of the two isomers was established by comparison with samples synthesised unequivocally (*vide infra*).

2-Methoxy-4:4'-dimethyldiphenyl sulphide was prepared by the reaction of *p*-thiocresol (12.4 g.) with 2-iodo-5-methylanisole (24.9 g.) as usual, and crystallised from ethanol in needles, m.p. 62-64° (23.4 g., 96%). (Found: C, 73.8; H, 6.7. $C_{15}H_{16}OS$ requires C, 73.8; H, 6.6 per cent).

2-Methoxy-4:4-dimethyldiphenylsulphone.—Oxidation of the foregoing sulphide with $KMnO_4$ in acetic acid medium furnished the *sulphone* (4.7 g., 85%). It crystallised from ethanol in rhombic plates, m.p. 131-32°. (Found: C, 64.7; H, 6.0. $C_{15}H_{16}O_3S$ requires C, 65.2; H, 5.8 per cent).

2-Hydroxy-4:4'-dimethyldiphenylsulphone was obtained by demethylation of the above compound and crystallised from ethanol as leaf-like crystals, m.p. 145-47°. (Found: C, 64.2; H, 5.1. $C_{14}H_{14}O_3S$ requires C, 64.1; H, 5.3 per cent).

4-Methoxy-2:4'-dimethyldiphenyl Sulphide.—The reaction of 4-methoxy-2-methylthiophenol (15.4 g.) and *p*-iodotoluene (21.9 g.) yielded the *sulphide* (90%), b.p. 242-44°/30 mm. (Found: C, 73.5; H, 6.7. $C_{15}H_{16}OS$ requires C, 73.8; H, 6.6 per cent).

4-Methoxy-2:4'-dimethyldiphenylsulphone was obtained in 90% yield by oxidation of the foregoing sulphide with $KMnO_4$ solution. It was also obtained (yield 80%) by the Friedel-Crafts reaction of 4-methoxy-2-methylbenzenesulphonyl chloride with toluene. It crystallised in needles from ethanol, m.p. 115-16°. (Found: C, 65.1; H, 5.8. $C_{15}H_{16}O_3S$ requires C, 65.2; H, 5.8

4-Hydroxy-2 : 4′-dimethyldiphenylsulphone was obtained in 80% yield by demethylation of the above sulphone. First it separated as an oil but solidified gradually. Crystallisation from ethanol gave needles, m.p. 151-52°. (Found : C, 64.0 ; H, 5.5. $C_{14}H_{14}O_3S$ requires C, 64.1 ; H, 5.3 per cent).

Fries Rearrangement of m-*Tolyl* o-*Toluenesulphonate*.—The usual procedure was adopted. The alkali-soluble product (9.5 g.) was extracted with hot benzene when a black brittle substance was left, and discarded. Evaporation of benzene furnished 7.5 g. (29% based on the sulphonate taken) of a mixture of *2-hydroxy-4 : 2′-* and *4-hydroxy-2 : 2′-dimethyldiphenylsulphones*. The separation of the two isomers was effected with hot ligroin in which the 4-hydroxysulphone was almost insoluble. The ligroin-insoluble portion (0.25 g.), on crystallisation from ethanol, gave plates, m.p. 162-64°. (Found : C, 63.9 ; H, 5.5. $C_{14}H_{14}O_3S$ requires C, 64.1 ; H, 5.3 per cent). The ligroin-soluble portion (7.25 g.) crystallised from ethanol as plates, m.p. 142-43°. (Found : C, 63.8 ; H, 5.2. $C_{14}H_{14}O_3S$ requires C, 64.1 ; H, 5.3 per cent). The two isomers were identified by comparison with samples synthesised unequivocally (see below).

2-Methoxy-4 : 2′-dimethyldiphenyl sulphide was prepared from 2-iodo-5-methylanisole and *o*-thiocresol in the usual way. It crystallised from ethanol in fine needles, m.p. 59-60°. (Found : C, 73.2 ; H, 6.6. $C_{15}H_{16}OS$ requires C, 73.8 ; H, 6.6 per cent).

2-Methoxy-4 : 2′-dimethyldiphenylsulphone.—Oxidation of the foregoing sulphide (2.44 g.) in glacial acetic acid with $KMnO_4$ solution afforded the *sulphone* (2 g., 73%), which crystallised from ethanol, m.p. 164-65°. (Found : C, 65.5 ; H, 5.9. $C_{15}H_{16}O_3S$ requires C, 65.2 ; H, 5.8 per cent).

2-Hydroxy-4 : 2′-dimethyldiphenylsulphone was obtained in 74% yield by demethylation of the above sulphone with HI. It crystallised from ethanol in plates, m.p. 142-43°. (Found : C, 63.8 ; H, 5.0. $C_{14}H_{14}O_3S$ requires C, 64.1 ; H, 5.3 per cent).

4-Methoxy-2 : 2′-dimethyldiphenyl sulphide was obtained from *o*-iodotoluene (21.9 g.) and 4-methoxy-2-methylthiophenol (Suter and McKenzie, *loc.cit.*) (15.4 g.) as before ; the yield was 22.5 g. (92%), b.p. 188-91°/13 mm. (Found : C, 73.6 ; H, 6.4. $C_{15}H_{16}OS$ requires C, 73.8 ; H, 6.6 per cent).

4-Methoxy-2 : 2′-dimethyldiphenylsulphone.—Oxidation of the foregoing sulphide afforded this *sulphone* in 82% yield. After crystallising from ethanol, it melted at 105-106°. (Found : C, 65.6 ; H, 6.0. $C_{15}H_{16}O_3S$ requires C, 65.2 ; H, 5.8 per cent).

4-Hydroxy-2 : 2′-dimethyldiphenylsulphone was obtained by demethylation of the foregoing sulphone in 87% yield. It crystallised from ethanol in plates, m.p. 163-64°. (Found : C, 64.0 ; H, 5.2. $C_{14}H_{14}O_3S$ requires C, 64.1 ; H, 5.3 per cent).

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COMPLEX COMPOUNDS OF COBALT^{III}. PART I. DIPYRIDINO-COBALTIC *bis*BIGUANIDINIUM HYDROXIDE AND ITS SALTS

By S. P. Ghosh and J. N. Gupta

Dipyridino-cobaltic *bis*biguanidinium complex has been prepared by the oxidation of cobaltous *bis*biguanidine in presence of pyridine. The dipyridino derivative was found to be more stable than the diamino derivative as it did not hydrolyse. The thiosulphate of this complex, like that of the hydroxo-aquo derivative, changed to μ-thiosulphato-*tetrakis*biguanide dithiosulphato-dicobalt. From the complex oxalate, the oxalato-oxalate has been obtained. From the reactions studied the complex was found to have a *trans* configuration. A series of salts, viz., sulphate, nitrate, thiosulphate, iodide, chlorobromide as well as the hydrated base have been prepared and their properties studied.

Diamino-cobaltic *bis*biguanidinium sulphate was prepared by Rây and Ghosh (this *Journal*, 1942, **19**, 1). It was found to hydrolyse in aqueous solution to hydroxo-aquo-cobaltic *bis*biguanidinium complex. The complexes were found to possess a *cis* configuration on the basis of their properties and reactions. The *trans* modification of the series was investigated by Rây and Majumdar (*ibid.*, 1946, **23**, 73). The present work was undertaken to ascertain the behaviour of pyridine in the formation of cobaltic *bis*biguanidinium complexes.

The dipyridino-cobaltic *bis*biguanidinium hydroxide was obtained in the same way as that of the diamino complex by the oxidation of the cobaltous *bis*biguanidinium hydroxide in presence of pyridine with the help of a brisk current of air. The dipyridino complex was, however, found to be more stable as it did not hydrolyse like the diamino compound. The diamino-cobaltic *bis*biguanidinium sulphate solution on prolonged treatment with air hydrolysed to the hydroxo-aquo complex, but the dipyridino complex remained stable for a long time, and raising the temperature decomposed the complex with the formation of the brownish black cobaltic oxide. Conductivity measurement of the complex nitrate also indicated only slight hydrolysis of the salt.

The behaviour of the dipyridino complex thiosulphate was analogous to that of the hydroxo-aquo-cobaltic *bis*biguanidinium thiosulphate as it transformed to the bright, insoluble, green, non-electrolyte binuclear bridge compound, μ-thiosulphato-*tetrakis*-biguanidinium dithiosulphato-dicobalt, in the presence of a trace of acetic acid or excess of sodium thiosulphate. Unlike the hydroxo-aquo-cobaltic *bis*biguanidinium thiosulphate, this reaction with dipyridino-*bis*biguanidinium-cobaltic thiosulphate could not be reversed in the presence of alkali.

In the case of a *cis* configuration, an oxalato complex was expected to be formed easily. The cobaltic oxalato-*bis*biguanidinium oxalate was, however, obtained as a decomposition product of the complex oxalate at an elevated temperature and in the presence of acid. It is quite possible that under such treatments a change into *cis* configuration first takes place and then the oxalato complex is formed. This indicates a *cis* configuration; probably the original substance is *trans* and is converted into its isomeric

cis form in the presence of H^+ ions. This view is also supported by the failure to easily prepare the oxalato derivative.

Besides the compounds discussed above, the sulphate, nitrate, iodide, hydroxide, chlorohydroxide and chlorobromide of the dipyridino-cobaltic *bis*biguanidinium complex have been prepared and their properies studied.

EXPERIMENTAL

Dipyridino-cobaltic-bis*biguanidinium Hydroxide*.—Cobaltous *bis*biguanidine was prepared by the action of strongly alkaline (NaOH) biguanide sulphate solution, in calculated quantity, upon a solution of cobalt chloride. It was washed free of alkali with cold water by decantation as rapidly as possible to avoid oxidation. The product was filtered and then treated with pure pyridine and oxidised by passing a brisk current of air through it. After several hours, a red solution with a few red crystals was obtained. There was a slight decomposition of the complex, indicated by the deposition of traces of the black cobalt oxide. The mixture was filtered through a quantitative filter paper. The filtrate on cooling deposited deep violet, permanganate-like crystals. The crystals were filtered out, washed with ice-cold water and alcohol and dried to a constant weight in CO_2-free air. The substance is soluble in water and reacts alkaline to litmus. {Found : N, 35.60; Co, 12.39. $[Co(Py)_2(BigH^+)_2](OH)_3$ requires N, 35.73; Co, 12.54 per cent}.

Cobaltic-dipyridino-bis*biguanidinium Sulphate*.—The red solution of the complex hydroxide on neutralisation with dilute H_2SO_4 deposited red crystals of the sulphate. A minute quantity of the cobaltic *tris*biguanidinium sulphate formed was removed by fractional crystallisation from water. Cobaltic *tris*biguanidinium sulphate was found to be more soluble. The pure crystals were washed with water and alcohol and dried in air. {Found : N, 24.85; SO_4, 21.59; Co, 9.00. $[Co(Py)_2(BigH^+)_2]_2(SO_4)_3$, 12 H_2O requires N, 25.04; SO_4, 21.46 ; Co, 8.80 per cent}. The substance almost completely lost the water of crystallisation at 120°; but there was a slight decomposition as was apparent from the smell of pyridine.

Cobaltic-dipyridino-bis*biguanidinium Thiosulphate*.—The red solution of the complex base was neutralised with dilute HCl. On adding a solution of $Na_2S_2O_3$ dropwise to this solution in the cold, the complex thiosulphate was immediately precipitated as red crystals. The substance was filtered at once, washed with cold water and alcohol and dried in air. {Found : Co, 9.28 ; S_2O_3, 26.30. $[Co(Py)_2(BigH^+)_2]_2(S_2O_3)_3.6H_2O$ requires Co, 9.20; S_2O_3, 26.21 per cent}.

When, however, an excess of $Na_2S_2O_3$ was used a green precipitate was obtained. The red thiosulphate slowly changed to the insoluble bright green variety in the presence of a trace of acetic acid also. The green product was washed with water and alcohol and dried in air. It did not contain any pyridine. {Found : Co, 13.23; S_2O_3, 37.68. $[Co_2(S_2O_3)_3(BigH^+)_4]$ requires Co, 13.18; S_2O_3, 37.58 per cent}. This compound was the μ-thiosulphato-*tetrakis*biguanidinium dithiosulphato-dicobalt, originally prepared by Rây and Ghosh (this *Journal*, 1942, **19**, 7).

Cobaltic-dipyridino-bis*biguanidinium nitrate* was precipitated as deep violet crystals when the base was neutralised with diiute HNO_3. The crystals were filtered with ice-cold water and alcohol, in which it was slightly soluble, and dried in air. The substance is readily soluble in water. {Found : Co, 9.85 ; NO_3, 31.63. $[Co(Py)_2(BigH^+)_2](NO_3)_3$ requires Co, 9.73 ; NO_3, 30.75 per cent}.

Equivalent conductivity of $[Co(Py)_2(BigH^+)_2](NO_3)_3$ *at* 35° ±.2.

Dilution (litres)	32	64	128	256	512	1024
Ωv	113.37	120.32	128.77	142.59	146.33	151.24
Ω_∞ (mean)	156.29					

$(1 + n_1 \times n_2.0.692.v)^{-\frac{1}{2}}$ where n_1 and n_2 are the valences of the cation and the anion.

In case of $[Co(NH_3)_2(BigH^+)_2]Cl_3.2H_2O$ the value for Ω 1024 was found to be 178.8 mohs at 33° (Rây and Majumdar, *loc. cit.*). The complex was found to hydrolyse to a large degree.

The equivalent conductivity of this salt can be compared with that of $La(NO_3)_3$ at 25° (Landdolt, Tabellen, 1923, II, p. 1090).

v (litres)	32	64	128	256	512	1024
Ωv	104.8	112.0	119.9	125.5	130 9	134 5

From this it can be inferred that the dipyridino complex hydrolyses to a very small degree in aqueous solution.

Cobaltic-dipyridino-bis*biguanidinium iodide* was prepared by the action of a concentrated solution of KI on that of the complex nitrate. The crystals separated on cooling in scarlet-red colour. The substance was recrystallised from water, washed with alcohol and dried in air. {Found : Co, 7.13 ; I, 45.30. $[Co(Py)_2(BigH^+)_2]I_3.2H_2O$ requires Co, 7.05; I, 45.46 per cent}. The substance is readily soluble in water and alcohol.

Cobaltic-dipyridino-bis*biguanidinium Chlorohydroxide*.—The solution of the complex base, when partly neutralised (p_H 8-9) with dilute HCl, furnished a violet precipitate. This was washed thoroughly with water and alcohol and dried to a constant weight in CO_2-free air. {Found: Co, 12.25; Cl, 7.00. $[Co(Py)_2(BigH^+)_2](OH)_2Cl.\frac{1}{2}H_2O$ requires Co, 11.86 ; Cl, 7.13 per cent}. The violet precipitate obtained at p_H 8-9 dissolved on adding more HCl to a clear violet solution, forming probably the normal chloride ; but this could not be isolated in a pure state due to high solubility.

Cobaltic-dipyridino-bis*biguanidinium monochlorobromide* was obtained by completely neutralising the complex base and then adding a strong solution of KBr. At first a few crops of orange-yellow cobaltic *tris*biguanidinium bromide were obtained and finally after standing for two days in cold the chlorobromide separated as red-violet long needles. The crystals were purified by recrystallisation from water and washed and dried as usual. {Found : Co, 9.1 ; total Ag halide, 78.25. $[Co(Py)_2(BigH^+)_2]ClBr_2.2H_2O$ requires Co, 9.01; total Ag halide, 79.8 per cent}.

Cobaltic-dipyridino-bis*biguanidinium oxalate* was prepared by neutralising the complex base with oxalic acid. The red crystals were filtered, washed with water and alcohol and dried in air. {Found : Co, 9.61 ; C_2O_4, 20.30. $[Co(Py)_2(BigH^+)_2]_2(C_2O_4)_3.8H_2O$ requires Co, 9.46; C_2O_4, 21.10 per cent}. The substance on heating at 95° decomposed with the loss of water and pyridine. It is soluble in water. The solution on heating slowly evolves pyridine and the colour changes to violet.

Cobaltic-dipyridino-oxalato-bis*biguanidinium Oxalate*.—A solution of the complex oxalate was heated at about 60° in presence of a little of H_2SO_4. The colour of the solution gradually changed from red to violet and pyridine was disengaged ; when the evolution of pyridine ceased the solution was cooled and deep violet crystals separated. These were filtered, washed and dried in the usual way. {Found : Co, 13.90 ; N, 31.9 ; C_2O_4, 29.4. $[Co(C_2O_4).(BigH^+{}_2]_2(C_2O_4)_3.4H_2O$ requires Co, 13.95 ; N, 32.6 ; C_2O_4, 30.77 per cent)}. This compound was also obtained from the hydroxo-aquo-cobaltic-*bis*-biguanidinium hydroxide hydrate by Rây and Majumdar (this *Journal*, 1946, **23**, 82). The compound is sparingly soluble in water. The compound could not be prepared by the action of excess of $Na_2C_2O_4$ on a hot solution of the normal oxalate. The complex decomposed giving a blue solution.

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SEPARATION OF METHYL ESTERS OF FATTY ACIDS FROM THEIR MIXTURES BY UREA COMPLEXES

By A. S. Gupta and J. S. Aggarwal

The separation of saturated and unsaturated acids from their mixtures by the urea-complex procedure is only of a qualitative nature and cannot be adopted as an analytical method.

Schlenk and Holman (*J. Amer. Chem. Soc.*, 1950, **72**, 5001) from their study on the urea-complex formation of binary mixtures of some fatty acids in methyl alcohol at 25° found that the separation was better when the difference in unsaturation and chain-length of the constituents was more, but separation into pure acids was not possible in any case. It was considered worthwhile to try the separation of the constituents of the binary mixtures of some common methyl esters of fatty acids using urea solutions in methyl alcohol of different concentrations and quantities and by fractional separation of urea complexes formed by the addition of urea in two or more stages.

Experimental

As the esters were found to furnish increased yields of urea complexes than the free fatty acids, methyl esters of the various acids having the following constants were employed in these experiments: stearic, m. p. 69°, M.W. 283.5; palmitic, m.p. 61.5°, M. W. 257; oleic, I. V. 87; linoleic, I. V. 187.

The mixtures of the acid esters were prepared by mixing equal quantities of the esters of two acids, one of them being saturated and the other unsaturated acid. The mixtures of acid esters were treated under various conditions with urea at 15°. After keeping overnight, each mixture was filtered through a sintered glass funnel and the crystals of the complexes were washed with petroleum ether (b. p. 40°-60°). The complexes were decomposed with HCl (dil., 1%). The separated fatty acids were recovered with petroleum ether (40°-60°) and isolated as usual. The solvents were completely removed from the raffinates and the washings, and after acidifying with HCl (dil.) the fatty acids were isolated as above. The amount of component esters in each fraction was calculated from its iodine value. The results with the mixtures of linoleic and stearic acid esters (1 : 1) are shown in Table I.

The solid urea complexes (1 g.), obtained from experiment 1 (Table I), were recrystallised from methyl alcohol (15 c.c.). After keeping overnight at 15°, the esters were isolated from the separated crystals; yield 59.5% on the total mixture (I. V. 28.3) affording the linoleic ester in the fraction as 16.4%. Recrystallisation of the above complexes lowered the yield of the esters in solid material to 36%, but the linoleic ester content was only 5.7%. When methyl alcohol, saturated with urea, was used for crystallisation of the solid complexes, the iodine value of the esters obtained from the crystallised product could not be at all reduced.

TABLE I

Separation of the components from the mixture of linoleic and stearic acid esters (1 : 1) by urea complexes.

No.	Urea (g.) and MeOH (c.c. per g. of the ester mixture).	Esters in complexes			Esters in raffinate.		
		Amount.	I.V. (Wijs).	Linoleic ester in the fraction.	Amount.	I.V. (Wijs).	Linoleic ester in the fraction.
1	12 in saturated solution *	74.33%	56.9	33.0%	24.52%	166.2	96.4%
2	3 ,, ,,	60.06	35.7	20.7	38.72	160.0	93.0
3	2.1 ,, ,,	48.26	28.4	16.4	50.46	156.3	90 6
4	12 in 80% MeOH saturated soln.	79.9	77.9	45.0	15.47	100.0	58 0
5	Urea : MeOH, 5 :7	89.0	75 7	43.9	9.48	161.2	93 5

* The saturated solution was prepared at room temperature (28°-32°) and contained about 20% urea, so the ratio of urea to MeOH was approximately 1 :5 in the solution.

The urea complexes obtained from saturated methyl alcohol (about 20% urea conc.) with some binary mixtures of saturated and unsaturated acid esters (1 g.) were recrystallised from methyl alcohol (10 c.c.). The characteristics of the esters obtained from the solid product are shown in Table II.

TABLE II

Composition of ester fractions from urea complexes of acid mixtures after crystallisation from methyl alcohol.

No.	Component of ester mixture	Urea added per g. of the ester mixtures in sat. soln.	Esters in crystallised complexes.		
			Amount.	I. V. (Wijs).	Unsaturated ester content in the fraction.
1	Steric-linoleic (1 :1)	12 g.	71.2%	50.1	29.0%
2	Palmitic-linoleic (1 :1)	12	70.8	55.3	32.1
3	Palmitic-oleic (1 :1)	12	72.4	37.2	43.5

Fractionation of Esters by addition of Urea in stages.—To 1 g. of the fatty acid ester mixture urea (2 g.) in methyl alcohol, just enough to make a saturated solution, was added. After keeping overnight at 15° the solid complexes (C_1) were removed and 2 g. of more urea was added to the raffinate and the second crop of complexes (C_2) formed in the usual manner was also separated. The esters were isolated from both the complexes and the last raffinate as usual. The characteristics of the various fractions obtained in the separation of the mixtures of (1) stearic-linoleic esters and (2) stearic-oleic esters are shown in Table III.

TABLE III

Composition of the fractions of esters formed by addition of urea in stages.

Ester fraction from	Stearic-linoleic esters (1 :1). Ester in the fraction.	I. V. (Wijs).	Linoleic ester in the fraction.	Stearic-oleic esters (1 :1). Ester in the fraction.	I. V. (Wijs).	Oleic ester in the fraction.
Complexes C_1	44.62%	28.7	16.7%	50.22%	23.0	26.8%
Complexes C_2	36.35	101.7	59.0	42.10	66.1	77.2
Raffinate	16.53	163.5	94.8	5.18	85.2	99.5

Separation of Esters by Urea-complex formation in dilute solution.—It has been observed before that unsaturated acids form solid urea complexes progressively in increasing amounts as the quantity of methyl alcohol used in their formation is decreased. With a view to ascertaining the effect of dilute solution of urea in methyl alcohol on the separation of esters, experiments were conducted with a mixture of stearic and linoleic esters (1 : 1). Different quantities of 10% urea solution in methyl alcohol were added to 1 g. samples of the above mixture and complexes were formed as usual at 15°. The esters were isolated from the solid complexes. Their quantities and composition are shown in Table IV.

TABLE IV

Separation of the mixture of stearic and linoleic acid esters (1 : 1) by complex formation in 10% urea solution in methyl alcohol.

No.	Urea soln. added per g. of the ester mixture.	Ester from complexes. Amount.	I. V. (Wijs).	Linoleic ester in the fraction.
1	24.6 g.	25.02 %	1.06	0.73%
2	100.5	44.75	2.10	1.80
3	138.7	45.81	2.80	1.65

CONCLUSION

The results of the separation of the components of the mixture of linoleic and stearic acid esters by urea complexes (Table I) are more or less in the similar lines as those of Schlenk and Holman (*loc. cit.*) who carried out the fractionation only in saturated solution of urea in methyl alcohol at 25°. If less urea is employed for complex formation, the amount of unsaturated component in the solid complex fraction decreases, but correspondingly smaller yield of the saturated ester is obtained. Crystallisation of the complexes from methyl alcohol does not reduce the unsaturated component appreciably (Table II). Unsaturated component of sufficient purity is obtained from the raffinate when the urea is added in two stages (Table III), but its amount is only of the order of 5 to 16.5% as against 50% present in the original mixture. A comparison of the results obtained in complex formation with a small quantity of solvent

(Table I, No. 5) and in presence of a larger amount of methyl alcohol (Table IV) is interesting. The separation into saturated and unsaturated constituents is very little in the former case, but methyl stearate of sufficient purity could be obtained from solid complexes in the latter set of experiments where a dilute solution of urea in methyl alcohol (10%) was employed. The recovery of the saturated ester out of solid complexes from a mixture of stearic and linoleic acid ester (1 : 1) in this case (Table IV), however, does not go above 45% even when 13.8 g. of urea is added per gram of the ester mixture. As expected, the separation is comparatively good when one of the components is of a higher unsaturation.

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EFFECT OF NON-ELECTROLYTES ON THE ANTAGONISM OF IONS IN COAGULATION OF HYDROPHOBIC SOL

By L. Pochhali and S. N. Mukherjee

The effect of the non-electrolytes, viz., methyl alcohol, ethyl alcohol, sucrose, glycerol and glycol, on the antagonism of KCl and $BaCl_2$ in coagulating arsenious sulphide sols has been studied. It has been found that the non-electrolyter which stabilise the sol increase the antagonism and those which sensitise the sol decrease it.

The coagulating power of ions in mixtures of electrolytes on colloidal solutions is not always additive as observed by different workers (Linder and Picton, *J. Chem. Soc.*, 1895, **67**, 67; Weiser, *J. Phys. Chem.*, 1921, **25**, 680; Freundlich and Scholz, *Koll.-Chem. Beih.*, 1922, **16**, 267; Mukherjee and Ghosh, this *Journal*, 1925, 1, 213, et seq). It has been observed that the total amount of coagulating ions in the case of electrolytic mixtures is sometimes greater than that of the individuals taken separately. Explanation offered for this ionic antagonism (as it is called) is based upon two fundamental assumptions: (*i*) the inhibiting influence of each coagulating ion on the adsorption of the other, and (*ii*) the stabilising action of the ions having the same charge as the sol (Fred Hazel, *J. Phys. Chem.*, 1941, **45**, 747). Ostwald and Hoffmann (*Kolloid. Z.*, 1937, **80**, 186), however, offered an explanation based on the activity coefficients of the coagulating ions, coagulating power being a function of the activity coefficients.

The influence of non-electrolytes on the stability of sols appears to be anomalous. The effect is one of sensitisation in some sols while stabilisation in others. Even the same non-electrolyte, when added to a particular sol, sometimes sensitises the sol towards a certain coagulating electrolyte, but stabilises it against another. The change in dielectric constant consequent upon addition of the non-electrolyte is certainly an influencing factor in such cases, but it alone is not sufficient to explain the facts observed (Lachs and Chwalinski, *Z. physikal. Chem.*, 1932, **A159**, 172). The influence of the non-electrolyte on the adsorption of both similarly as well as oppositely charged ions should also be taken into consideration.

In the light of the above, non-electrolytes are expected to have some influence also on the antagonism of ions in the phenomenon of coagulation of colloids, and hence, the question of ionic antagonism in presence of non-electrolytes has been reopened.

Experimental

The system studied was the arsenious sulphide sol with the pair of electrolytes, potassium and barium chlorides (the strong antagonistic effect of which is well known). The effects of different non-electrolytes, viz., methyl alcohol, ethyl alcohol, glycol, glycerol and sucrose, in different concentrations have been observed with different concentrations of the coagulating electrolytes.

The arsenious sulphide sol was prepared by mixing equal volumes of a half-saturated solution of arsenious oxide and water, saturated with hydrogen sulphide, and then by passing hydrogen sulphide through the mixture till there was no arsenious oxide left in it. The excess of hydrogen sulphide was driven off with a current of hydrogen gas.

For determining the coagulating concentrations of electrolytes, light from a single-filament lamp was allowed to pass through a layer of definite thickness of the mixture of the sol and electrolytes, placed at a constant distance from the source of light, and the time noted when the sharp outline of the filament just disappeared. The intensity of light was kept constant by passing a constant current through the filament, as shown by a sensitive ammeter. Electrolytes or mixtures of electrolytes are considered to have equi-coagulating concentrations when the time required for reaching the same stage of coalescence is the same in each case. In each case, to 5 c.c. sol was added the mixture of electrolyte solutions, non-electrolytes or water, as the case may be, keeping always the total volume at 10 c.c. The whole mixture was then poured into a glass vessel having rectangular sides and kept at the fixed position at a definite distance from the source of light. The mode of addition of the electrolyte mixture to the sol and mixing was always the same, as any variation affected the results to a considerable extent.

TABLE I

[Coagulating conc. of KCl and $BaCl_2$ in m. moles/litre]

% Conc. of non-electrolytes.	Methyl alcohol.		Ethyl alcohol.		Sucrose.		Glycerol.		Glycol.	
	KCl	$BaCl_2$.	KCl.	$BaCl_2$.	KCl.	$BaCl_2$.	KCl.	$BaCl_2$.	KCl.	$BaCl_2$.
0	57.5	2 8	60.0	2.8	55.0	3 0	63.5	2.9	6.1	3.0
2.5	...	...	...	...	54.0	3.0	...	...	...	...
5	70.0	2.4	65.0	3.4	57.5	3.0	...	...	...	...
10	92.5	2.0	70.0	4.0	62.5	3.4	62.0	2.4	6.2	2.5
20	95.0	1 8	85.0	4.4	...	...	64.0	2.2	6.1	2.2

From Table I we find that in the case of methyl alcohol, the arsenious sulphide sol is stabilised towards coagulation by KCl, but is sensitised towards $BaCl_2$. Glycerol and glycol have no effect towards coagulation by KCl, but sensitise the sol towards coagulation by $BaCl_2$. The highest stabilising effect is observed in the case of ethyl alcohol, both towards KCl and $BaCl_2$. Sucrose appears to have a very small stabilising effect to both the electrolytes.

TABLE II

Antagonism of ions in pure aq. medium

% Coagulating conc. of						
KCl	...	0	20	40	60	80
$BaCl_2$	...	100	119	111	86	57
Total	...	100	139	151	146	137

TABLE III

% Coagulating conc. of KCl.	% Coagulating conc. of $BaCl_2$.	Total	% Coagulating conc. of KCl.	% Coagulating conc. of $BaCl_2$	Total
MeOH (10%).			MeOH (20%).		
0	100	100	0	100	100
27	135	162	26	125	151
54	115	169	53	114	167
81	20	101	79	68	147
EtOH (10%).			EtOH (20%).		
0	100	100	0	100	100
29	140	169	29	164	193
57	110	167	57	136	193
86	35	121	86	55	141
Sucrose (5%).			Sucrose (10%).		
0	100	100	0	100	100
26	131	157	24	135	159
52	107	159	48	118	166
78	53	131	72	71	143
Glycerol (10%).			Glycerol (20%).		
0	100	100	0	100	100
24	108	132	23	102	125
48	98	146	47	91	138
73	62	135	70	63	133
Glycol (10%)			Glycol (20%)		
0	100	100	0	100	100
24	116	140	25	112	137
49	105	154	50	96	146
73	67	140	74	54	128

In Tables II and III the results of observations on ionic antagonism in presence of different non-electrolytes have been shown. Amounts of the electrolytes in the mixture have been shown in percentages of their coagulating concentrations when used separately (as from Table I). The total percentage clearly shows the extent of antagonism. Had there been no antagonism, the total should have come out to be exactly 100. As for example in Table II (2nd row), the mixture of electrolytes containing 20% of the coagulating concentration (0.0550 *M*) must have 119% of the coagulating concentration of $BaCl_2$ (0.0028 *M*) to coagulate the sol.

Two salient points emerge from the above tables (Tables II and III): (1) The antagonism is maximum near about 50% of the coagulating concentration of KCl; at lower or higher KCl-concentration, the coagulating power of $BaCl_2$ increases and the antagonism decreases. (2) The non-electrolytes, which stabilise the sol, show increased antagonism and those which sensitise the sol decrease the antagonism.

Ethyl alcohol stabilises the sol more than any of the other non-electrolytes, both towards KCl and $BaCl_2$, and in this case the antagonism is maximum. Sucrose can slightly stabilise the sol towards both the electrolytes and in this case the antagonism

is slightly higher than that in the pure aqueous medium. Although glycerol and glycol have no appreciable effect on the coagulation of the sol by KCl, they sensitise the sol towards coagulation by $BaCl_2$, and here the antagonism is lower than that in the pure aqueous medium. Methyl alcohol stabilises the sol towards KCl, but sensitises it towards $BaCl_2$. 20% Methyl alcohol increases the coagulating concentration of KCl by 65% but decreases that of $BaCl_2$ by 36% only. So it is expected that the antagonism in presence of 20% methyl alcohol will be greater than that in the pure aqueous medium, and this is borne out by the experimental results.

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REDUCTION OF MERCURIC CHLORIDE BY OXALIC ACID IN THE DARK IN PRESENCE OF POTASSIUM PERMANGANATE AS INDUCTOR

By C. Prasad and Abani K. Bhattacharya

The reaction between $HgCl_2$ and $H_2C_2O_4$, induced by $KMnO_4$, has been studied from the viewpoint of the concentration effect of the inductor on the induction period and the extent of reduction of mercuric chloride. The induction period has been found to remain almost constant up to a certain concentration of $KMnO_4$, beyond which it gradually goes on increasing till MnO_2 is precipitated when it becomes difficult to ascertain it. By increasing the concentration of the inductor, the reduction of $HgCl_2$ increases, but its reduction per mole of $KMnO_4$ at first increases rapidly and then gradually decreases. These observations suggest that the reduction of mercuric chloride is brought about through the mechanism of heterogeneous catalysis due to the activation of reacting molecules on the surface of colloidal MnO_2, formed in the $KMnO_4-H_2C_2O_4$ reaction.

The reduction of $HgCl_2$ by $H_2C_2O_4$, induced by $KMnO_4$, had been studied in the past by many workers (Dhar, *Proc. K. Acad. Amsterdam*, 1920, **23**, 308; Skrabal, *Z. anorg. Chem.*, 1904, **42**, 1; Launer, *J. Amer. Chem. Soc.*, 1932, **54**, 2597; Lidwell and Bell, *J. Chem. Soc.*, 1935, 1303). Recently Weiss ("Discussions", Faraday Soc., 1947) has discussed a mechanism of this reaction based on the formation of Mn^{3+} ions and $C_2O_4^-$ radical. Adamson (*J. Phys. Coll. Chem.*, 1951, **55**, 293) has, from his studies on the kinetics of the manganous-permanganate reaction, given a very critical opinion on the mechanism suggested by Weiss and others.

Weiss observed an induction period in the reduction of $HgCl_2$ by oxalic acid in presence of $KMnO_4$; he referred to its importance but did not study its relation with the concentration of the inductor. We have therefore attempted to investigate this aspect of the reaction and studied the reduction of $HgCl_2$ with different initial concentrations of $KMnO_4$.

Experimental

Standard solutions of mercuric chloride, oxalic acid, potassium permanganate, etc. were prepared from A. R. Chemicals, in redistilled water. The reactants were mixed together in conical flasks (same size) set up in an electrically regulated thermostat. The time interval between the mixing of the reactants and the first appearance of calomel precipitation was noted and designated as the 'induction period'.

For determining the amount of reduction of mercuric chloride in the dark, the reaction vessels, covered with black photographic paper, were similarly arranged. Total reduction of $HgCl_2$ was determined by pipetting out a definite volume of the reaction mixture with the help of a cotton plug into a known excess of KI solution and then back-titrating the residual KI by $M/20$-$HgCl_2$. The titre volume was further corrected by a titration error curve (Kolthoff and Stenger, "Volumetric Analysis", Vol. I, p. 156) and the reduction of $HgCl_2$ was calculated.

Induction Period

When $KMnO_4$ is added to a dilute solution containing $HgCl_2$ and oxalic acid, the reduction of mercuric chloride to mercurous state does not start immediately, but reduction is observed to begin after a certain time when the mixture becomes brown or colorless. This time interval is termed the 'induction period' and is connected with the mechanism of reduction of mercuric chloride.

Table I shows the relationship between the concentration of $KMnO_4$ in the reaction mixture containing constant concentrations of $HgCl_2$ and $H_2C_2O_4$, and the induction period.

TABLE I

Temp = 35°. $(HgCl_2)_0 = (H_2C_2O_4)_0 = 6.667 \times 10^{-2}$ g. mol./litre.

Conc. of $KMnO_4$.	Induction period.	Colour of soln. when the Hg_2Cl_2 formation starts.
0.1667×10^{-3} equiv./litre	7.5 min.	Almost colorless
0.3333	8	Do
0.6666	8	Light brown
1.3333	8	Do
3.3330	8	Do
5.3330	9	Brown
6.6666	10	Do
10.0	18	Black due t MnO_2 ppt.
13 3333	>24 hrs.	Do

From Table I the induction period does not appear to change appreciably by increasing the concentration of $KMnO_4$ up to a certain limit, beyond which it starts increasing gradually for such concentrations of the inductor as make the precipitate of MnO_2 appreciably visible. When the concentration of $KMnO_4$ is equivalent to that of oxalic acid, much MnO_2 is precipitated and the induction period cannot be determined within 24 hours.

It was further observed that the induction period for a reaction mixture ($HgCl_2 = H_2C_2O_4 = 6.667 \times 10^{-2}$ g. mol./ litre ; $KMnO_4 = 0.3333 \times 10^{-2}$ g. equiv./litre) was 19 mins. at 25° and 8 mins. at 35°. Hence, the induction period appears to depend on the concentration of $KMnO_4$ as well as on the temperature of the reaction.

TABLE II

Relationship between the amount of $KMnO_4$ *added and the extent of reduction of mercuric chloride.*

Temp. = 35°. $(HgCl_2)_0 = (H_2C_2O_4)_0 = 6.667 \times 10^{-2}$ g. mol /litre.

$(KMnO_4)_0$.	$HgCl_2$ (reduced).	$\frac{HgCl_2 \text{ (reduced)}}{(KMnO_4)}$	$(KMnO_4)_0$.	$HgCl_2$ (reduced).	$\frac{HgCl_2 \text{ (reduced)}}{(KMnO_4)}$
0.1667 mol./litre $\times 10^{-3}$	1.333 mol./litre $\times 10^{-3}$	8.0	3.333 mol./litre $\times 10^{3}$	15.33mol./litre $\times 10^{3}$	4.6
0.25	3.333	13.3	5.0	15.83	3.17
0.3333	5.1	15.3	6.667	17.17	2.575
0.5	7.333	14.67	8.333	18.0	2.16
0.6667	8.5	12.75	10.0	19.83	1.98
1.667	12.33	7.4			

From Table II the total reduction of $HgCl_2$ appears to increase with increasing concentration of $KMnO_4$. It is further observed that the reduction of $HgCl_2$ per mole of $KMnO_4$ rapidly increases in the beginning but slows down afterwards. This suggests that some $KMnO_4$ becomes ineffective in inducing the reduction of mercuric chloride in the later stages.

Probable Mechanism

In view of the observations recorded in Table I, we are of the opinion that the first stage of the reduction starts in the formation of highly dispersed MnO_2 sol. The reduction of $HgCl_2$ is then brought about by the activation of the molecules on the surface of colloidal MnO_2. In other words, the induction takes place through the energy of surface catalysis, and hence, the primary stage of activation and the subsequent reduction of $HgCl_2$ appear to be governed by a heterogeneous mechanism. The heterogeneous character of this reaction (in its initial stage) is supported by the observations on the period of induction in Table I. It has been observed that there is very little increase in the induction period within the concentrations of $KMnO_4$ 0.1667 – 6.6666 equiv./litre $\times 10^{-2}$. But on adding more of permanganate, MnO_2 is precipitated and the induction period also increases appreciably. This suggests a sudden decrease in the surface due to the precipitation of the MnO_2 sol at higher concentrations of $KMnO_4$. Under such condition longer time would be required by the oxalic acid to bring the precipitated MnO_2 to the optimum stage of dispersion at which the activation of $HgCl_2$ or $H_2C_2O_4$ or of both takes place. The induction period is therefore bound to increase according to this heterogeneous mechanism of activation.

The temperature effect on the induction period also supports the theory of heterogeneous mechanism in the primary stage of the reaction. If it is assumed that molecules are activated by thermal effects, it is obvious that the rate of activation of molecules due to surface catalysis will be greater at 35° than that at 25°, and this has actually been observed.

This view is further supported by the fact that when different amounts of colloidal MnO_2 are added to a mixture of $HgCl_2$ and $H_2C_2O_4$, the induction period is almost the same, and very much less (hardly 2-3 minutes) while the extent of reduction of $HgCl_2$ increases with higher concentrations of colloidal MnO_2, as observed with $KMnO_4$ an inductor.

In the quantitative study of the total reduction of $HgCl_2$, it has been observed that the reduction continues for a pretty long time even when the brown colour of the solution has been completely discharged. At the colorless stage, it appears that the highly dispersed MnO_2 has been dissolved by oxalic acid, releasing Mn^{2+} ions which act as catalyst in this reaction (vide Dhar, *J. Chem. Soc.*, 1917, **111**, 695). Hence, the whole mechanism of this reaction, in all probability, is a phenomenon of heterogeneous cum homogeneous catalysis, the primary stage being the surface activation of the reactant molecules followed by the catalytic influence of Mn^{2+} ions during the later stages.

Previous workers (Weiss and others, *loc.cit.*) have explained this reaction by chain mechanism initiated through the formation of Mn^{3+} and $C_2O_4^-$. While we do not argue against their mechanism, the fact remains that the formation of Mn^{3+} and $C_2O_4^-$ at tem-

peratures of 25° and 35° is more hypothetical than the mechanism of surface activation and catalytic influence of Mn^{2+} ion, suggested by us. It may further be stated that there is hardly any reference in the literature regarding the temperature at which Mn^{3+} ion can remain stable. It appears from the behaviour of manganic salts that they are very unstable at ordinary temperatures, and hence, any mechanism based on the formation of Mn^{3+} ion and $C_2O_4^-$ radical seems to be conflicting with the stability of these ions.†

In view of many other factors, which are known to play their role in this reaction, it may prove a helpful guide to study its kinetics in the catalysed state and determine the apparent order, temperature coefficient and activation energy.

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STUDIES ON THE GELATION OF SILICIC ACID SOLS. PART III. CATIONIC AND ANIONIC EFFECTS ON THE TIME OF GELATION

By K. C. Sen and B. N. Ghosh

The addition of electrolytes does not bring about coagulation of silicic acid sols but lowers the time of gelation. In the region of p_H lower than that corresponding to the maximum time of gelation, the greater the valency of the cation used, the greater is the lowering of the time of gelation. At higher p_H, the effect of the valency of the cations on the gelation time becomes less and less pronounced. The behaviour with the anions is just the reverse. In each acid system the electric charge of the colloid is negative in the region of p_H beyond that corresponding to the maximum time of gelation. At lower p_H, the particles are positively charged.

It has been reported (Hurd *et al.*, *J. Phys. Chem.*, 1933, **37**, 321 ; 1934, **38**, 663) that the addition of electrolytes affects the time of gelation of silicic acid sols, prepared by using acetic acid. This is perhaps not a consequence of coagulation. Some of the electrolytes are likely to influence the time of gelation mainly by altering the p_H. The time of gelation, as influenced by the addition of some electrolytes, has therefore been studied in some detail.

Experimental

Sols prepared by using hydrochloric acid were used. To the freshly prepared sols known quantities of electrolytes were added; the silica contents of the sols were always kept at 3.0%, but the electrolyte concentrations were varied. The p_H of the mixtures was then noted. The time of gelation of these sols was determined at 55°.

It is found that at a particular p_H, the greater the concentration of the added electrolyte, the lower is the time of gelation. Comparison of the time of gelation (t) of sols containing 2.0N concentrations of NaCl, $CaCl_2$ and $AlCl_3$ with that of the sol to which no extra amount of electrolyte has been added, is shown in Fig. 1. It appears from the curves that although the p_H corresponding to the maximum time for gelation is not appreciably affected, the value of this time is considerably lowered. Thus 2.0 N concentrations of $AlCl_3$, $CaCl_2$ and NaCl have reduced the maximum time of gelation by about 63%, 52% and 31% respectively. At about p_H 1.8 and upwards, the effect of all the three electrolytes is of the same order. Thus at p_H 2.0, concentrations (2.0 N) of the electrolytes reduce the time of gelation by about 60%. The specific effect of the added electrolytes becomes more pronounced at lower p_H. Thus, the concentrations of $AlCl_3$, $CaCl_2$ and NaCl at 2.0 N level reduce the time of gelation by about 52%, 40% and 10% respectively at 0.5 p_H, 55%, 47% and 21% respectively at 0.8 p_H, and 60%, 51% and 30% respectively at 1.0 p_H. It can therefore be concluded from the curves that the cations of higher valence reduce the time of gelation to a greater extent in the region of lower

p_H, but this effect becomes progressively less as the p_H increases. It also appears from experimental data that the specific effects of Ba^{2+} and Ca^{2+} ions are almost of the same order.

FIG. 1

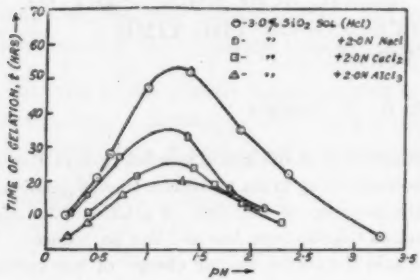
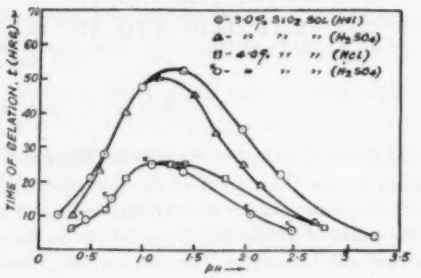


FIG. 2



The influence of anions on the time of gelation may be observed by comparing the experimental data obtained with hydrochloric and sulphuric acid systems. The graphical representation of the data in Fig. 2 clearly illustrates the anion effect. At p_H lower than that corresponding to the maximum time of gelation, the effect of the valency of the anions is negligible, whereas at a higher p_H a marked anion effect is noticeable. These observations are just the reverse of what has been found in the case of the cations.

Electric Charge.—The anion and the cation effects described above naturally bring in the question of electrical charge on the particles of silicic acid. Measurements of the electrical charge have therefore been made by the electroendosmotic method used by Mukherjee (*Nature*, 1922, **110**, 732) and Ghosh (*J. Chem. Soc.*, 1926, 2609; 1927, 1250). Sometimes after gelation, when syneresis had started, the gel mixture was centrifuged. The lower part of the U-tube was then filled with the centrifuged gel which formed the diaphragm. The upper part of the U-tube and the side tubes were then filled with the supernatant liquid. The movement of the air bubble in the horizontal bent tube connecting the side tubes was noted. If the air bubble moves to the negative electrode, the colloid is positively charged and *vice versa*. It is found that in each acid system, the electrical charge of the colloid is negative in the region of p_H beyond that corresponding to the maximum time of gelation. At lower p_H region the particles are positively charged. Near about the maximum time of gelation, it is likely that the particles possess no charge at all or they are only slightly charged.

If the cation and the anion effects are the results of either adsorption or coagulation, the differentiation between the cations would have been prominent in the negative region and that between the anions in the positive region. The experimental facts, however, are contrary to this expectation. Moreover, the maximum time of gelation, which signifies greater stability of the sol, occurs at or near about a point where the electrical charge of the particles is perhaps zero. Adsorption or coagulation appears therefore to play a secondary role, if any, in the process of gelation of silicic acid sols.

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SEARCH FOR NEW ANTIBACTERIAL COMPOUNDS. PART I

By S. S. Tiwari and Brajendra N. Tripathi

Several 2-chloro-4-*tert.*-butylphenol esters of saturated fatty acids have been converted into the corresponding *o*-hydroxyketones by the Fries rearrangement. These have been reduced by the Clemmensen reduction to the corresponding 2-chloro-4-*tert.*-butyl-6-alkylphenols, which may be active antibacterials.

Baichwal, Jhaveri and Khorana (*J. Sci. Ind. Res.*, 1951, **10A**, 498) observed that introduction of an alkyl or a halogen substituent in the phenol increased its activity. In a mono-substituted phenol the position of an alkyl group is not important. The bactericidal activity increases with the increase in the length of the alkyl chain up to a certain limit, beyond which activity falls. The maximum activity is reached at different levels for different micro-organisms. But when halogen and alkyl groups are both present in phenol, the consideration of the relative positions becomes important. Klarmann *et al.* (*J. Lab. Clin. Med.*, 1934, **19**, 835 ; 1934, **20**, 40) showed that *p*-alkyl derivatives of *o*-chlorophenol were efficient germicides. As regards the nature of the alkyl chain in the case of xylenols, the activity against *Staph. aureus* increases more rapidly with branched chain compounds, and in the cases of dihydroxy derivatives, branched chain compounds have been reported to possess unusually high activity (Baichwal *et al.*, *loc. cit.*). Keeping these facts in view, we have prepared various 2-chloro-4-*tert.*-butyl-6-alkylphenols which may possess much enhanced microbial potency.

Several saturated fatty acid esters of 2-chloro-4-*tert.*-butylphenol have been prepared by the action of appropriate acid chloride on the phenol, following the usual procedure (Tiwari and Tewari, this *Journal*, 1954, **31**, 79). These esters were converted into the corresponding *o*-hydroxyketones by the Fries rearrangement, and the latter on the Clemmensen reduction furnished various 2-chloro-4-*tert.*-butyl-6-alkylphenols. The work on the evaluation of their bacteriostatic activity is in progress.

Experimental

*Esters of 2-Chloro-4-*tert.*-butylphenol.*—Eight new esters prepared are summarised in Table I.

Table I

Esters.	B.P.	Yield.	Mol. formula.	% Carbon. Found.	% Carbon. Calc.	% Hydrogen. Found.	% Hydrogen. Calc.
Acetate	180°/10 mm.	80%	$C_{12}H_{15}O_2Cl$	63.24	63.57	7.12	6.62
Propionate	129°/10	72	$C_{13}H_{17}O_2Cl$	64.45	64 86	7.24	7.07
Butyrate	162°/16	70	$C_{14}H_{19}O_2Cl$	65.22	66 01	7.15	7.47
Valerate	169°/21	74	$C_{15}H_{21}O_2Cl$	66.71	67.05	8.37	7.82
Caproate	157°/10	76	$C_{16}H_{23}O_2Cl$	68 47	67 97	8 06	8 14
Caprylate	187°/10	68	$C_{18}H_{27}O_2Cl$	69.17	69.56	8.91	8 70
Capriate	200°/12	70	$C_{20}H_{31}O_2Cl$	71.45	70.91	8.73	9.16
Laurate	212°/10	63	$C_{22}H_{35}O_2Cl$	72.22	72 02	9.07	9.55

TABLE II

o-Hydroxyketones and their 2 : 4-dinitrophenylhydrazone derivatives.

2-Chloro-4-*tert.*-butylphenol esters.	2-Hydroxy-3-chloro-5-*tert.*-butyl-	B.P.	Yield.	Analysis of ketone.				2 :4-Dinitrophenylhydrazone			
				% Carbon. Found.	Calc.	% Hydrogen. Found.	Calc.	M.P.	Mol. formula.	% Nitrogen. Found.	Calc.
Acetate	Acetophenone	142°/33 mm.	85%	63.41	63.57	6.91	6.62	224°	$C_{18}H_{15}O_5N_4Cl$	13.98	13.78
Propionate	Propiophenone	142°/10	80	64.42	64.86	7.52	7.07	227°	$C_{19}H_{17}O_5N_4Cl$	13.21	13.32
Butyrate	Butyrophenone	152°/10	80	66.50	65.01	7.67	7.47	176°	$C_{20}H_{23}O_5N_4Cl$	13.40	12.89
Valerate	Valerophenone	154°/20	75	67.44	67.05	7.91	7.82	185°	$C_{21}H_{25}O_5N_4Cl$	13.02	12.48
Caproate	Caprophenone	163°/13	71	68.21	67.97	8.56	8.14	163°	$C_{22}H_{27}O_5N_4Cl$	12.60	12.11
Caprylate	Caprylophenone	170°/10	72	69.82	69.56	8.52	8.70	127°	$C_{23}H_{31}O_5N_4Cl$	11.79	11.42
Caprate	Capriophenone	162°/13	68	71.31	70.91	9.54	9.16	185°	$C_{26}H_{35}O_5N_4Cl$	10.94	10.80
Laurate	Laurophenone	180°/22	68	72.40	72.02	9.12	9.55	193°	$C_{28}H_{39}O_5N_4Cl$	10.74	10.24

Fries Rearrangement of the Esters.—A mixture of ester (1.0 *M*) and $AlCl_3$ (anhyd., 1.5 *M*) was gradually heated to 110° and the *o*-hydroxyketone was isolated as usual (Tiwari and Tewari, *loc. cit.*). The *o*-hydroxyketones, so obtained, conformed to the characteristic tests of these ketones (Coulthard, Marshall and Pyman, *J. Chem. Soc.*, 1930, 280). The *o*-hydroxyketones were further characterised by their 2:4-dinitrophenylhydrazones which were recrystallised from glacial acetic acid (see Table II).

Clemmensen Reduction of 2-Chloro-4-tert.-butyl-6-acylphenols.—A mixture of zinc wool (20.0 g.), mercuric chloride (2.0 g.), HCl (conc., 5.0 c.c.) and water (20.0 c.c.) was stirred vigorously for 10 minutes. The supernatant liquid was then decanted off and the amalgamated zinc was liberally washed with water. It was covered by 30 c.c. of ethanol and 5.0 g. of *o*-hydroxyketone, and 10 c.c. of HCl (conc.) was added to it. The mixture was refluxed on a water-bath for 8 to 10 hours, during which 2 c.c. portions of HCl (conc.) were added after each hour.

After the period a drop of the liquid did not produce blue colour on a filter paper previously sprayed with aqueous ferric chloride. This indicated the absence of the *o*-hydroxyketone. Ethanol was then distilled off and the liquid was saturated with sodium chloride and extracted with ether. The ethereal extract was dried over anhydrous sodium sulphate and the ether removed by distillation. The product was then fractionally distilled. The various alkylphenols so obtained are summarised in Table III.

TABLE III

[R = 2-hydroxy-3-chloro-5-*tert.*-butyl-; P = 2-chloro-4-*tert.*-butylphenol]

o-Hydroxy-ketones	Chloroalkyl-phenol	B.P.	Yield.	Mol. formula.	% Carbon. Found.	% Carbon. Calc.	% Hydrogen. Found.	% Hydrogen. Calc.
R-acetophenone	6-Ethyl-P	139°/29mm.	64%	$C_{12}H_{17}OCl$	67.91	67.78	8 41	8.00
R-propiophenone	6-*n*-Propyl-P	119°/21	62	$C_{13}H_{19}OCl$	68.42	68.87	8.60	8.39
R-butyrophenone	6-*n*-Butyl-P	146°/11	58	$C_{14}H_{21}OCl$	69.71	69.85	8.83	8.73
R-valerophenone	6-*n*-Pentyl-P	163°/42	62	$C_{15}H_{23}OCl$	71.13	70.73	9.45	9.04
R-caprophenone	6 *n*-Hexyl-P	150°/12	58	$C_{16}H_{25}OCl$	71.00	71.51	9.78	9.31
R-caprylophenone	6-*n*-Octyl-P	153°/11	52	$C_{18}H_{29}OCl$	72.64	72.86	10.20	9.78
R-capriophenone	6-*n*-Decyl-P	150°/11	52	$C_{20}H_{33}OCl$	73.78	73.95	10.60	10.17
R-laurophenone	6-*n*-Dodecyl-P	170°/11	50	$C_{22}H_{37}OCl$	75.41	74 91	10 11	10.50

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SEARCH FOR NEW INSECTICIDES. PART II

By S. S. Tiwari and Brajendra Nath Tripathi

Several alkyl- and halogen-substituted phenolic esters of chloroacetic acid and the corresponding *o*-hydroxyketones, obtained on rearrangement, and 2-allyloxy-4 : 5-dimethyl-α-furophenone have been prepared with a view to studying their insecticidal activity.

The derivatives of chloroacetic acid are known to be potent insecticides. Hence, we prepared six chloroacetates of different phenols by the action of chloracetyl chloride on the appropriate phenols, following the method of Spasov (*Ann. Univ. Sofia*, 1938-39, **2**, 35, 289). Most of the phenols taken were halogen-substituted as Dowmal, Delvaux and Dills (*J. Econ. Entomol.*, 1950, **43**, 915) found that the chlorination of phenol derivatives increased the insecticidal efficiency.

Martin and Wain (*Nature*, 1944, **154**, 514) have suggested that the liberation of hydrochloric acid is the cause of the insecticidal efficiency of D. D. T. Chloroacetophenone readily produces hydrogen chloride (Fieser and Fieser, "Organic Chemistry", 2nd Ed., p. 686); thus the chloroacetyl group may act as powerful poisonous component for insects. Keeping this in view, we have prepared six *o* hydroxyketones by the Fries rearrangement of the above esters at 110° without solvent. Because of their *o*-hydroxyketonic nature, the phenolic groups of these compounds are in the chelated form, and hence, their lipoid solubility should be more than that of the corresponding parent phenol. The ketonic group itself being lipophilic in nature adds to the lipoid solubility. As the phenols themselves are toxic compounds, these compounds containing additional toxophore and having more lipoid solubility should be better contact insecticides (Laugger, Martin and Muller, *Helv. Chim. Acta*, 1944, **27**, 918).

Gilman *et. al.* (*Iowa State College J. Sci.*, 1932, **6**, 439 ; 1933, **7**, 419) have shown that α-furoates are good insecticides. Hence, considering that α-furoyl group may be an insect poisonous component, we prepared 2-allyloxy-4 : 5-dimethyl-α-furophenone by the etherification (Chen and Somerford, *J. Amer. Chem. Soc.*, 1951, **73**, 4694) of 2-α-furoyl-3 : 4-dimethylphenol, described earlier (Tiwari and Tripathi, this *Journal*, 1954, **31**, 841). This compound possesses allyl group as toxophore, ether linkage and ketonic group having lipophilic properties (Chen *et. al.*, *loc. cit.*) and α-furoyl group as an additional insect poisonous component. Thus, it may be a potent insecticide. The work on their insecticidal activity is in progress.

Experimental

Esters of Chloroacetic Acid.—The esters of chloracetic acid prepared are summarised in Table II.

TABLE I

o-Hydroxy-ω-chloroacetophenones and their 2:4-dinitrophenylhydrazones.

Ester.	Hydroxyketone.	B. P.	% Yield.	2:4-Dinitrophenylhydrazone. % Carbon.		% Hydrogen.		M. P.	Mol. formula.	% Nitrogen.	
				Found.	Calc.	Found.	Calc.			Found.	Calc.
2-Bromo-P	3-Bromo-A	174°/40 mm.	40.0	38.45	38 50	2.92	2.40	207°	$C_{14}H_{10}O_5N_4ClBr$	13.41	13.04
3-Ethyl-P	4-Ethyl-A	160°/37	76.0	60.12	60.45	5.04	5.54	194°	$C_{16}H_{15}O_5N_4Cl$	15.22	14.79
4-Bromo-P	5-Bromo-A	164°/35	80.0	38.43	38.50	2.79	2.40	215°	$C_{14}H_{10}O_5N_4ClBr$	13.44	13.04
2:4-Dichloro-P	3:5-Dichloro-A	128° (m.p.)	82.0	40.47	40.09	1.84	2.09	192°	$C_{14}H_9O_5N_4Cl$	13.69	13.36
2-Chloro-*tert.*-butyl-P	3-Chloro-5-*tert.*-butyl-A	180°/41	86.0	54.62	55.18	5.77	5.36	195°	$C_{18}H_{18}O_5N_4Cl$	12.48	12.70
3:4-Dimethyl-P	4:5-Dimethyl-A	164°/38	86.0	60.19	60.45	5.84	5.54	210°	$C_{16}H_{15}O_5N_4Cl$	14.69	14.79

[P = phenyl chloroacetate; A = 2-hydroxy-ω-chloroacetophenone].

TABLE II

No.	Esters.	B. P.	% Yield.	Mol. formula.	% Carbon. Found.	% Carbon. Calc.	% Hydrogen. Found.	% Hydrogen. Calc.
1	2-Bromo-P*	135°/11 mm.	68.0	$C_8H_6O_2ClBr$	38.80	38.50	2.82	2.40
2	3-Ethyl-P	128°/10	88.0	$C_{10}H_{11}O_2Cl$	60.13	60.45	5.97	5.54
3	4-Bromo-P	139°/11, 36°(m.p.)	76.0	$C_8H_6O_2ClBr$	38.22	38.50	2.76	2.40
4	2:4-Dichloro-P	143°/12	73.0	$C_8H_5O_2Cl_3$	39.57	40.09	2.51	2.09
5	2-Chloro-4-*tert.*-butyl-P	142°/11	74.0	$C_{12}H_{14}O_2Cl_2$	54.77	55.18	5.07	5.36
6	3:5-Dimethyl-P	135°/12	82.0	$C_{10}H_{11}O_2Cl$	60.93	60.45	5.27	5.54

* P = phenyl chloroacetate.

Fries Rearrangement of the Esters.—The ester (1.0 *M*) was rearranged by 1.1 *M* anhydrous aluminium chloride, and the *o*-hydroxyketone was isolated by following the usual method (Tiwari and Tewari, this *Journal*, 1954, **31**, 79). The content left after distillation of the *o*-hydroxyketone in the first two cases was worked up for the *para* isomer, which was found to be absent. The *o*-hydroxyketones, so obtained, gave violet coloration with alcoholic ferric chloride and afforded crystalline red precipitate with dilute caustic soda, thus conforming to Pyman's tests of the *o*-hydroxyketones (*J. Chem. Soc.*, 1930, 280). These *o*-hydroxyketones and their 2:4-dinitrophenylhydrazones are summarised in Table I.

2-Allyloxy-4:5-dimethyl-α-furophenone.—A mixture of 2-hydroxy-4:5-dimethyl-α-furophenone (3.0 g.), allyl bromide (2.0 g.), freshly fused potassium carbonate (4.0 g.) and acetone (50.0 c.c.) was refluxed on a water-bath for 10 hours. Soon after the refluxing started a heavy precipitate of potassium bromide began to separate. After the period the contents were cooled, mixed with water and extracted with ether. The ethereal extract was washed successively with 5% caustic soda solution and water and finally dehydrated over anhydrous sodium sulphate. The ether was removed by distillation and the residual oil distilled under reduced pressure, b. p. 163°/22 mm., yield 2.4 g. (Found: C, 75.48; H, 6.64. $C_{16}H_{16}O_3$ requires C, 75.0; H. 6.25 per cent).

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THE PHASE-DIAGRAM STUDIES OF THE BINARY SYSTEMS. PART II. SALOL-DIPHENYL, SALOL-ACENAPHTHENE AND SALOL-PHENANTHRENE

By D. K. Majumdar

The studies of the phase-diagrams of the binary systems of salol with diphenyl, acenaphthene and phenanthrene have disclosed formation of simple eutectics of all the three systems and there is no existence of any chemical union between them. Application of the Clapeyron equation reveals very slight departure from ideal solutions.

In a previous communication of the series (Majumdar and Rakshit, this *Journal*, 1955, **32**, 157) the studies of the phase-diagram of salol-naphthalene have been reported. The present investigation deals with freezing point-composition curves of the binary systems of salol with three other hydrocarbons, viz., diphenyl, acenaphthene and phenanthrene, from their thermal analysis. Each of these mixtures of salol and hydrocarbons readily begins to liquefy even at ordinary temperature and it would be of interest to investigate if any chemical change is involved therein.

Literature records very few such studies with salol, and these have been referred to in the previous communication. With the hydrocarbons, mentioned above, there are several binary systems which have been studied (Lee and Warner, *J. Amer. Chem. Soc.*, 1935, **57**, 318; Klochko-Zhovnir, *J. Appl. Chem. U.S.S.R.*, 1949, **22**, 848) and eutectic systems have been shown to exist with the exception of the systems acenaphthene and some nitro compounds (Efremov *et al.*, *Bull. Acad. Sci., U.S.S.R.*, 1936, 515; *J. Russ. Phys. Chem. Soc.*, 1927, **59**, 373).

Experimental

The materials used were chemical reagent varieties of B.D.H. The purity was checked always by freezing point determination by means of cooling curves. The data corresponded with the internationally accepted values. A point should, however, be noted regarding phenanthrene. The sample of phenanthrene used was recrystallised several times, and the constant m.p. was 99.2°. But the solution of phenanthrene in alcohol exhibited some fluorescence in actinic rays, which might be due to contamination with traces of anthracene. Further purification was not possible. Solid solution of anthracene in phenanthrene was known and the sample of phenanthrene of maximum purity obtained by Cohen and Cormier (*J. Amer. Chem. Soc.*, 1930, **52**, 4363) had the m.p. 99-99.5°. Phenanthrene obtained by us was therefore taken as the purest available.

The experimental procedure was the same as followed in our previous studies (*loc. cit.*). Only in some of our experiments, particularly with phenanthrene, the cooling was effected slowly in a paraffin bath of somewhat lower temperature, instead of the air-jacket of the Dewar flask. The usual corrections for supercooling and exposed stem of the thermometer were made.

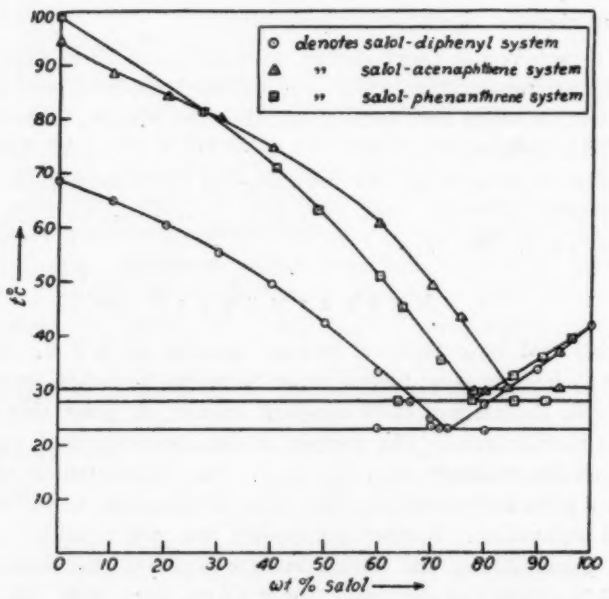
Salol-diphenyl.—The data of freezing points for various compositions are recorded in Table I and the corresponding plot in Fig. 1.

TABLE I

Wt. % of salol.	Freezing point. Initial.	Final.	Wt. % of salol.	Freezing point. Initial.	Final.	Wt. % of salol.	Freezing point. Initial.	Final.
100	42.0°	42.0°	71	...	23.38°	40	49.56°	
90	33.62°	...	70	24 98°	23.40°	30	55.43°	
80	27.19°	23.38°	66	28.00°	...	20	60.50°	
73	23.38°	23.38°	60	33.52°	23.38°	10	64.97°	
72	...	23.38°	50	42.79°	...	0	68.94°	68.94°

In the temperature-composition graph there is one single point which is a minimum and where the liquidus from either side meet the solidus. The system therefore admits of no chemical union but behaves as a simple eutectic. The eutectic point is 23.38° and the corresponding composition is 73% salol and 27% diphenyl by weight. The eutectic point has been confirmed by taking a mixture of the above-mentioned composi-

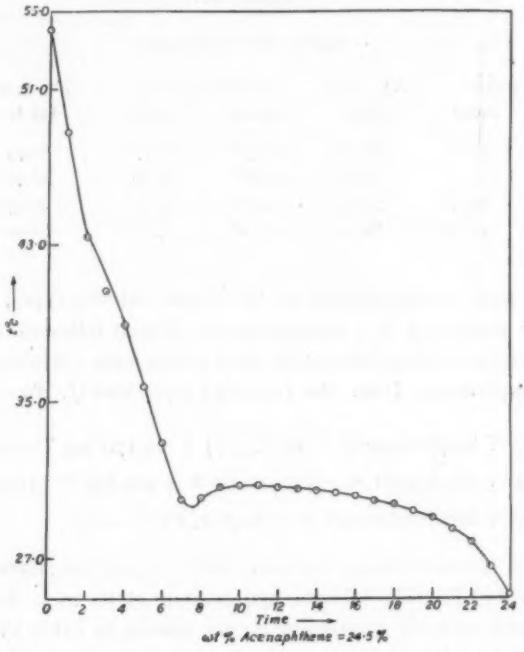
FIG. 1



tion which melts and freezes at the same temperature as noted above. It has also been corroborated by the fact that the second arrest point in time-temperature (cooling) curves also corresponds to the same temperature 23.38°. This latter fact shows further that the two components would not form a solid solution. Besides, the crystals separating in the initial stages of cooling above the eutectic temperature, on the right and left sides of the eutectic point, were pure salol and diphenyl respectively, verified from their

melting points. The solidified mixtures of different compositions also begin to melt at the same temperature, clearly proving the eutectic nature. A cooling curve is shown in Fig. 2 to show the nature of the arrest points.

FIG. 2



Salol-acenaphthene.—The mixture, having the eutectic composition of 84.1% salol and 15.9% acenaphthene by weight, indicated by the intersection of the liquidus curves, freezes at 30.37°. The freezing temperatures for various compositions are shown in Table II and the corresponding plot in Fig. 1.

TABLE II

Salol-acenaphthene.

Wt. % of salol.	Freezing point. Initial.	Final.	Wt. % of salol	Freezing point Initial.	Final.	Wt % of Initial.	Freezing point. salol.	Final.
100	42.00°	42 0°	78.7	33.42°	30 2°	40.0	74·59°	
94.0	36.95°	30.37°	75.5	43.68°		30 0	80.07°	
84.1	30.37°	30.37°	70.0	49·44°		20.0	84.20°	
80.0	...	30.0°	60 0	60 43°		10.0	88.50°	
						0	94·70°	94·7°

That there is no appreciable solubility of the components in the solid state has been proved by isolating the primary crystals of acenaphthene and salol. The constancy of the second arrest point for almost all the mixtures studied also excludes the possibility of any appreciable solid solution.

Salol-phenanthrene.—This system has a eutectic composition of 78.06% salol and 21.94% phenanthrene by weight, and a freezing temperature 28.26°. The freezing points for various mixtures are recorded in Table III and the corresponding plot in Fig. 1.

TABLE III

Salol-phenanthrene.

Wt. % of salol.	Freezing point. Initial.	Final.	Wt. % of salol.	Freezing point Initial.	Final.	Wt. % of salol.	Freezing point Initial.	Final
100.00	42 0°	42.0°	80.21	28 27°	28.27°	60.74	51 10°	
96.55	39.2°	...	78.06	28.26°	28.26°	48.78	63.19°	
91.26	36.28°	26.97°	71.82	35.60°	27.22°	40.57	71.10°	
85.75	32.87°	28.22°	64.50	45 12°	27.9°	26.91	81.55°	
						0	99.2°	99.2°

Phenanthrene-salol system belongs to the simple eutectic type ; the absence of solid solution has been confirmed in a manner similar to that followed in other two systems. The ideal solubilities have been calculated, after taking into consideration, the variation of $\triangle H_f$ with temperature, from the following equations (*J. Amer. Chem. Soc.*, 1935, **57**, 318) :

$$\log N \text{ (naphthalene)} = (518.9/T) + 19.170 \log T - 0.0115\, T - 46.253$$

$$\log N \text{ (diphenyl)} = -(274.0/T) + 4.380 \log T - 10.299$$

$$\log N \text{ (phenanthrene)} = -(945.2/T) + 2.540$$

In the case of phenanthrene, however, $\Delta H_f = 4325$ cal./mole (Hodgman, "Hand Book of Chemistry and Physics") for the hydrocarbon at its m.p. has been used. The ideal solubilities and eutectic temperatures are shown in Table IV (see also Majumdar and Rakshit, *loc. cit.*). In calculating eutectic temperatures, use has been made of the equation,

$$\log N = -\frac{\Delta H_f}{2.303R}\,[(1/T)-(1/T^\circ)],$$

where N stands for the mole fraction of salol at eutectic composition and ΔH_f, its molar latent heat of fusion at its melting point. This calculation is approximate to the extent that variation of ΔH_f for salol with temperature is not known and has not been taken into account.

TABLE IV

Systems.	Eutectic composition. Mole. fraction (salol). Expt.	*Ideal.	Eutectic temperature. Expt.	Calc. from ΔH_f of salol.
Salol-naphthalene	0 7158	0.6888	25.49°	21.5°
Salol-diphenyl	0.6606	0.6050	23.38°	20.2°
Salol-acenaphthene	0.7920	...	30.37°	29.1°
Salol-phenanthrene	0.7476	0.7471	28.26°	26.1°

*Calc. from ΔH_f of hydrocarbons.

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STUDIES ON METAL FERROCYANIDES. PART I. VOLUMETRIC DETERMINATION OF CADMIUM BY FERROCYANIDE

By G. S. Deshmukh and M. Venugopalan

Precipitations with ferrocyanide solutions of varying concentrations have been carried out with different concentrations of the metal salt solutions. From a study of the various complex metal ferrocyanides formed, the possibility of quantitative determination of metals by ferrocyanide precipitation is suggested.

The present determination of Cd is based on the quantitative precipitation of the complexes $K_2CdFe(CN)_6$ and $3K_2CdFe(CN)_6.Cd_2Fe(CN)_6$, with dilute and moderately strong solutions of potassium ferrocyanide The accuracy of the determination appears to lie within the limits of phase changes of the different complexes.

Formation of complexes of cadmium and ferrocyanide has been reported by earlier workers (Williams, "Cyanogen Compounds", 1948, p 181 ; Tananaev and Kozlov, *Zhur. Anal. Khim.*, 1951, **6**, 149 ; Belcher, Nuttan and Stephen, *J. Chem. Soc.*, 1951, 3444). According to them the composition of the different complexes formed, depends on the concentration of the cadmium and ferrocyanide solutions. Review of literature, however, shows that the p_H of the medium as also the presence of non-interfering electrolytes stabilises many of the complexes. During studies in these laboratories on different metal ferrocyanides, it was observed that the addition of cadmium chloride solution of varying concentrations to an excess of freshly prepared potassium ferrocyanide solution containing a non-interfering electrolyte like potassium chloride led to the precipitation of $K_2CdFe(CN)_6$ and $3K_2CdFe(CN)_6.Cd_2Fe(CN)_6$, the former with dilute solutions and the latter with moderately strong solutions of ferrocyanide. The present authors have worked out the amount of cadmium that can be determined by the present method.

Experimental

A stock solution of $CdCl_2$ was prepared by dissolving a known quantity of B. D. H., A. R. quality $CdCl_2$ in water. The weight of Cd in this solution was determined by the iodine method (Thompson and Mellor, "A Treatise on Quantitative Inorganic Analysis", 1938, pp. 180, 376). Pure (Merck sample) potassium ferrocyanide solutions of different concentrations, varying from 1 to 4% were prepared and exact concentrations determined by titrations with standard ceric sulphate (Willard and Young, *J. Amer. Chem. Soc.*, 1933, **55**, 3260). A standard solution of ceric sulphate was prepared by the method of Meyer and Aufrecht (*Ber.*, 1904, **37**, 140).

A known quantity of the cadmium solution was pipetted into a 250 c.c. flask, and a known excess of potassium ferrocyanide solution added. About 50 c.c. of a 2% solution of KCl was added, the volume made up to 250 c.c. and kept aside overnight with frequent shaking. The precipitate was filtered through Whatman No 50. First few c.c. of the filtrate containing excess of ferrocyanide was thrown off after rinsing the flask

and 50 c.c. of the filtrate was pipetted out, 20 c.c. of 4-5N-H_2SO_4 and a drop of phenanthroline ferrous complex as indicator were added to it and titrated against a standard ceric sulphate solution. A preliminary titration of a known quantity of ferrocyanide was carried out against the standard ceric sulphate solution.

Different concentrations of the ferrocyanide, varying from 4 to 1% solution, were tried and the accuracy of the method for different concentrations of cadmium worked out. For the titration relationship the precipitate appears to have the composition $CdK_2Fe(CN)_6$ and $3CdK_2Fe(CN)_6$. $Cd_2Fe(CN)_6$ or $Cd_3K_6[Fe(CN)_6]_4$ according as concentrations of 1% and 2-4% of ferrocyanide solutions used. A typical set of results is shown in Table I.

TABLE I

$CdCl_2$ soln.	Conc. of ferrocyanide.	Wt. of Cd by ferrocyanide.	Wt. of Cd by I_2 method.	Diff.
5 c.c.	50 c.c. of 1% soln	0.02701 g.		0.00004
	25 2 ,,	0.02699	0.02705 g.	0.00006
	25 4 ,,	0.02699		0.00006
10	50 1 ,,	0.05395		0.00016
	50 2 ,,	0.05395	0.05411	0.00016
	25 4 ,,	0.05395		0.00016
15	75 1 ,,	0.08042		0.00074
	50 2 ,,	0.08091	0.08116	0.00025
	25 4 ,,	0.07993		0.00123
20	75 1 ,,	0.10900		0.00090
	75 2 ,,	0.10900	0.10810	0.00090
	25 4 ,,	0.10690		0.00120
25	100 1 ,,	0.13700		0.00170
	75 2 ,,	0.13700	0.13530	0.00170
	50 4 ,,	0.13280		0.00250
30	100 1 ,,	0.15990		0.00243
	50 4 ,,	0.15990	0.16233	0.00243

The results show the variation of the complex with the variation in concentration of the alkali ferrocyanide. With the ferrocyanide solution of 4 to 2% strength, the formation of the complex $Cd_3K_6[Fe(CN)_6]_4$ afforded quantitative determination of Cd, whereas solutions of 1% strength precipitated the complex $CdK_2Fe(CN)_6$ only. It is thus inferred that the concentration of the alkali ferrocyanide plays an important part in the formation of Cd-ferrocyanide complexes.

The precipitate and the solution have to be kept standing for a definite time, say 12 hours, and it is essential to add some non-interfering electrolytes, such as KCl, to allow the precipitated complex to settle and also to increase the size of the particles (to prevent the passing down of the fine precipitate through a filter). Whatman No. 50 filter was found most suitable for the purpose.

The formation of the complexes mentioned above, under the conditions specified, have been supported by the conclusions of earlier workers (*loc. cit.*).

Apart from the accuracy of this new volumetric procedure for the determination of Cd, its essential advantage lies in the use of ceric sulphate as a standard titrant, for the indirect titration of ferrocyanide.

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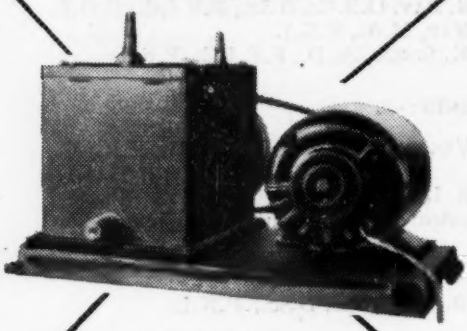

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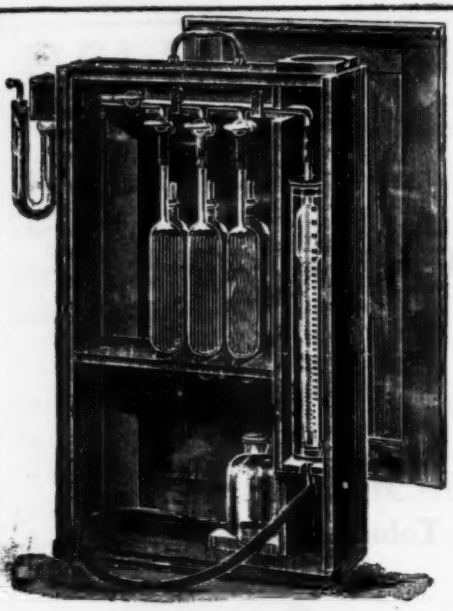

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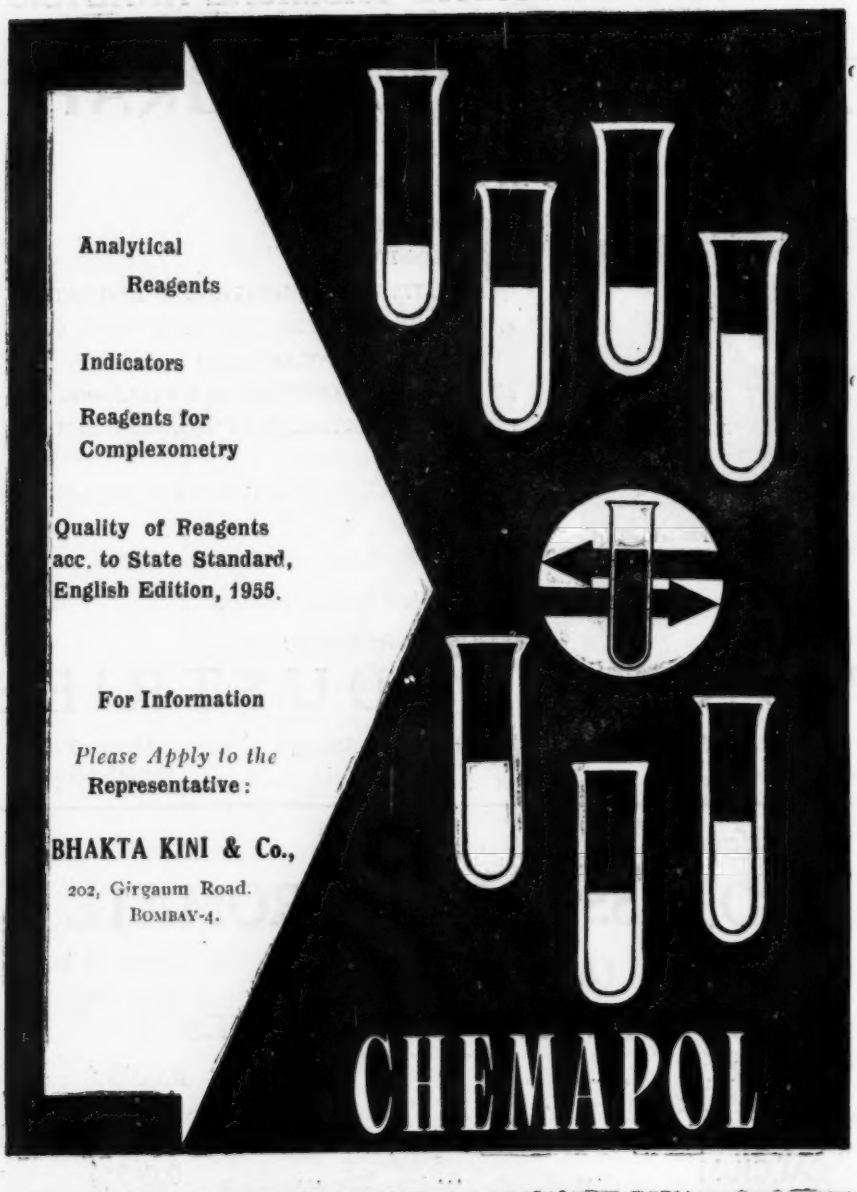

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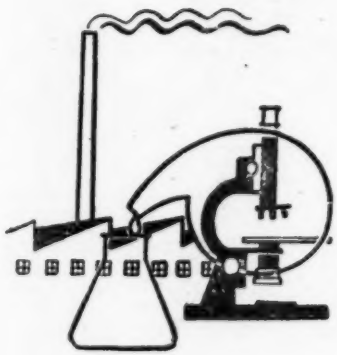

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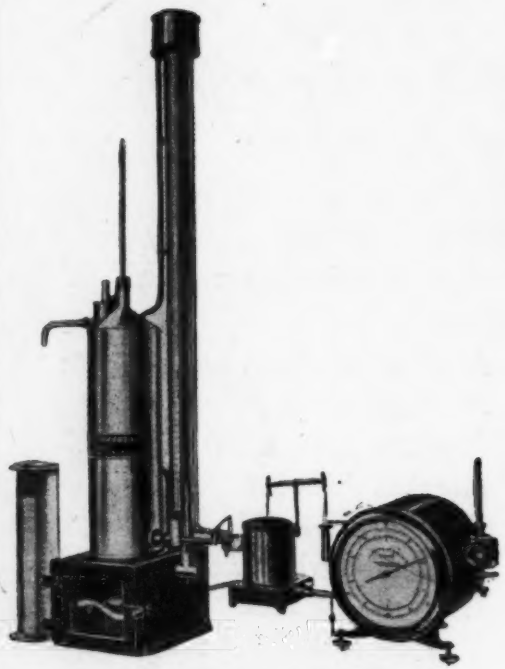

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